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RECENT DEVELOPMENTS IN DESULFURIZATION OF FUEL OIL AND WASTE GAS IN JAPAN (1972)

PREPARED BY

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16. Abstracts

Desulfurization of fuel oil and stack gas is assuming growing importance in Japan as a result of the mounting imports of high-sulfur crude oil. This report describes the recent developments in desulfurization in Japan up to December 1971. The following aspects of the developments are described: emission and regulation of SO_2 in Japan; outline of the recent developments; desulfurization of heavy oil; waste-gas desulfurization by wet process; waste-gas desulfurization by dry process; and economic aspects.

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Recent Developments in Desulfurization of Fuel Oil and Waste Gas in Japan (1972)

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Foreword

Desulfurization of fuel oil and stack gas is assuming growing importance in Japan in parallel to the mounting imports of high-sulfur crude oil. Japan today may well be most advanced in the world in the practice of desulfurization. For 19 commercial plants for hydrodesulfurization of heavy oil and many commercial plants for stack-gas desulfurization are already in operation in Japan, where various new processes including gasification desulfurization of fuel oil are being developed.

A salient feature of desulfurization efforts in Japan is that they are oriented toward processes that yield salable by-products such as sulfur, sulfuric acid, sodium sulfite and high-quality gypsum. This is because Japan is subject to limitations in domestic supply of sulfur and its compounds as well as in land space available for disposal of useless by-products. As desulfurization is making rapid progress, however, it will not be long before supply of the by-products runs far ahead of demand. A flue-gas desulfurization plant using a wet-lime process is under construction as the first large plant which does not produce salable by-products.

The present paper describes the recent developments in desulfurization in Japan up to December 1971.

January 1972

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Recent Developments in Desulfurization of Fuel Oil and Waste Gas in Japan (1972)

Contents

1 Emission and regulation of SO_2 in Japan

- 1.1 Supply of energy
- 1.2 Oil and its sulfur content
- 1.3 Heavy oil and sulfur
- 1.4 Other fuels
- 1.5 Policy for sulfur abatement
- 1.6 Environmental standard
- 1.7 Emission standard

2 Outline of recent developments in desulfurization

- 2.1 Hydrodesulfurization of heavy oil
- 2.2 Waste-gas desulfurization
- 2.3 Government policy for development of desulfurization technology

3 Desulfurization of heavy oil

- 3.1 UOP-RCD Isomax process for topped-crude hydrodesulfurization
- 3.2 Gulf process for topped-crude hydrodesulfurization
- 3.3 MDS process for topped-crude hydrodesulfurization
- 3.4 Other tests on topped-crude hydrodesulfurization
- 3.5 Vacuum gas-oil hydrodesulfurization
- 3.6 Production of fuel gas by gasification desulfurization of heavy oil (Ube process)
- 3.7 Power generation by gasification desulfurization of heavy oil (Japan Gasoline process)

4 Waste-gas desulfurization by wet process

- 4.1 Kureha process (sodium scrubbing)
- 4.2 Showa Denko process (ammonia or sodium scrubbing)
- 4.3 Bahco-Tsukishima process (sodium scrubbing)
- 4.4 Kanagawa PIL process (Jinkoshi process)
- 4.5 Oji process (sodium scrubbing)

4.6 Wellman-Lord process (MKK)
4.7 Wellman-Lord process (SCE)
4.8 Mitsubishi-JEC process (lime-gypsum process)
4.9 Chiyoda Thoroughbred 101 process
4.10 Kawasaki magnesium process
4.11 Grillo process
4.12 Chemico process (lime scrubbing and magnesium scrubbing)
4.13 Takahax process (H_2S recovery)
4.14 Other wet processes

5 Waste-gas desulfurization by dry process
5.1 Mitsubishi DAP-Mn process
5.2 Hitachi activated carbon process
5.3 Sumitomo activated carbon process
5.4 NRIPR active sodium carbonate process
5.5 Shell process (Cupric oxide process)
5.6 Other dry processes

6 Economic aspects
6.1 Supply, demand, and price of sulfur and its compounds
6.2 Cost of hydrodesulfurization
6.3 Cost of flue gas desulfurization
6.4 Cost comparison of oil desulfurization and flue-gas desulfurization

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Abbreviations

BPSD:	Barrels per stream day	Nm^3/hr:	Normal cubic meters per hour
kl:	Kiloliters	SCF:	Standard cubic feet
l:	Liters	sec.:	Seconds
LHSV:	Liquid hourly space velocity	t or tons:	Metric tons
MW:	Megawatts	TC:	Topped crude
		VGO:	Vacuum gas oil
		¥:	Yen

1 Emission and regulation of SO_2 in Japan

1.1 Supply of energy

Along with the rapid industrial advances in Japan demand for energy here is mounting steadily. Supply of energy doubled in the past five years (Table 1.1); most of the increase was accounted for by imported oil. In 1970, 71% of the total energy supply depended upon petroleum while in 1965 the dependence was 58%. Hydraulic power and coal are not increasing so rapidly. Even though atomic power may eventually supplant petroleum, demand for petroleum is thought to keep growing for some time to come. Per-capita energy consumption in Japan was one-fifth that in the United States in 1965, one-fourth in 1968, and most likely close to one-third in 1970. Japan's energy consumption is expected to continue a fairly rapid growth(Tables 1.1, 1.2).

Table 1.1 Supply of primary energy (10^{10}kcal)[1, 2)]

	1960	1965	1970	1975
Electric power				
Hydraulic	14,328	18,722	19,620	21,200
Atomic	0	9	1,122	10,200
Coal				
Domestic	32,229	31,637	25,209	22,600
Imported	6,702	13,580	39,224	62,700
Oil				
Domestic	587	740	847	800
Imported	34,782	95,964	218,914	342,500
Natural gas				
Domestic	927	2,008	2,676	2,900
Imported (LNG)	0	0	1,298	4,500
Other energy sources	4,194	2,924	1,918	1,700
Total	93,749	165,614	310,468	470,400

Table 1.2 Total capacity of electric power plants (MW)[1)]

	1960	1965	1970	1980
Hydraulic	12,678	16,275	20,405	32,900
Fossil fuel	10,946	24,702	46,931	91,200
Atomic	0	13	1,336	27,000
Total	23,634	40,990	68,312	151,100

1.2 Oil and its sulfur content

With very little domestic production of petroleum, Japan depends on overseas supplies for more than 99% of its oil consumption. Petroleum is imported here mostly in the form of crude oil and partly fuel oil. About 85% of the crude oil comes from the Middle East (Table 1.3). Middle East crude is rich in sulfur; Khafji crude, especially, contains as much as 2.6% sulfur, as against the average 1.6% for all imported crudes. The total amount of sulfur present in imported crude and fuel oil exceeded 3 million tons in 1970 (Table 1.4).

Table 1.3 Crude oil imports and their sources (in millions of kiloliters)[1)]

District	1965	1967	1969	1970
Middle East	77.4	114.1	152.5	173.3
Far East	6.2	8.3	19.5	27.5
U. S. S. R.	2.9	1.7	0.6	0.6
Other districts	1.1	1.0	2.0	3.5
Total	87.6	125.1	174.6	204.9

According to the Government's petroleum supply plan for 1971 through 1975, demand for oil is expected to reach approximately 230 million kiloliters in 1971 and 390 million kiloliters in 1975. Even though efforts have been made to import low-sulfur oil, the amount of sulfur seems to grow steadily (Table 1.4).

Table 1.4 Estimated imports of oils and their sulfur content[3)]

	Import of crude oil (million kl)	Average sulfur content (%)	Sulfur from crude oil (1,000t)	Import of fuel oil (million kl)	Sulfur from fuel oil (1,000t)	Total sulfur (1,000t)
1970	205	1.56	2,757	24	324	3,081
1971	232	1.46	2,912	23	302	3,214
1972	244	1.36	2,853	39	532	3,385
1973	273	1.36	3,194	44	599	3,793
		(1.26)	(2,960)			(3,559)
1974	302	1.36	3,536	51	682	4,217
		(1.16)	(3,016)			(3,698)
1975	332	1.36	3,884	55	730	4,614
		(1.06)	(3,027)			(3,757)

1.3 Heavy oil and sulfur

In Japan, most of crude oil is treated by topping (atmospheric distillation). The residual oil from topping is known as "heavy oil" and is used for fuel. From 100 parts crude, 55 parts heavy oil is obtained on the average. Approximately 90% of the sulfur in crude remains in heavy oil. Heavy oil from Khafji crude has a sulfur content as high as 4% (Figure 1.1).

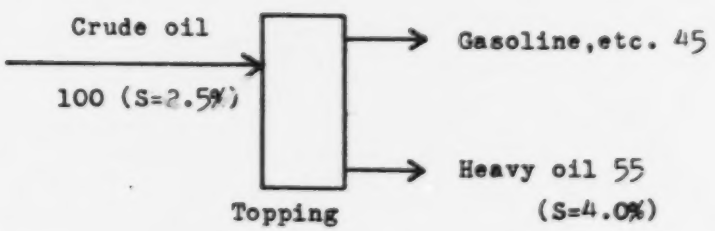


Figure 1.1 Rough material balance in topping of Khafji crude

Consumption of heavy oil amounted to approximately 50 million kiloliters in 1965 and to 110 million kiloliters in 1970 (Table 1.5). In 1970 about one-fourth of the heavy oil was subjected to hydrodesulfurization giving nearly 300,000 tons of sulfur as by-product. Still 2.5 million tons of sulfur in heavy oil burned produced 5 million tons of SO_2, which constituted the chief source of SO_2 emission. About a third of heavy oil was burned in electric power stations and the rest in other plants and buildings.

Table 1.5 Consumption of heavy oil (in thousands of kiloliters)[1)]

Use	1965	1967	1969	1970
Electric power	11,862	18,963	29,809	34,745
Chemical industry	5,762	7,297	8,529	12,657
Steel industry	5,256	7,109	9,267	11,445
Ceramic industry	6,017	8,051	9,716	10,352
Other uses	20,933	28,632	39,794	44,615
Total	49,830	70,052	97,115	113,814

1.4 Other fuels

Domestic production of coal is decreasing because coal is more expensive than oil (Table 1.6). About a half of domestic coal has been burned in power plants (Table 1.7). The coal mined in Japan contains about 1% sulfur on the average. Imported coal, which has been increasing, is used to produce coke for the iron industry. The SO_2 problem is much less with coal than with heavy oil.

Table 1.6 Production and import of coal (in thousands of tons)[1)]

	1965	1967	1969	1970
Production	55,642	51,512	46,389	40,851
Import	17,637	27,213	43,260	50,941

Table 1.7 Consumption of fuels for electric power[1)]

	1965	1967	1969	1970
Heavy oil (1,000kl)	11,862	18,963	29,809	34,745
Crude oil (1,000kl)	719	2,192	3,939	7,251
Coal (1,000t)	20,909	26,349	24,363	18,826
Natural gas(million Nm^3)	39	5	4	60

Japan produces little natural gas (Table 1.8). Liquefied natural gas (LNG) has been imported since 1969 as a means of alleviating the SO_2 problem (Tables 1.8, 1.7). Two LNG tankers, each with a capacity of 30,000 tons, are in service between Alaska and Japan. Four more similar tankers are under construction to bring LNG from Brunei. Several power plants in big cities have started to use LNG, although it is much more expensive than oil (Table 6.4).

Table 1.8 Production and import of natural gas[1)]

	1965	1967	1969	1970
Production(million Nm^3)	2,108	2,328	2,721	2,808
Import (LNG, 1,000t)	0	0	182	976

1.5 Policy for sulfur abatement

A report published by the Comittee for Sulfur Dimishing Policy, Ministry of International Trade and Industry, indicates that to decrease the SO_2 level to the environmental standard by 1978 sulfur in fuel has to be diminished as shown in Table 1.9.

Table 1.9 Fuel consumption and SO_2 level in 1967 and need for low-sulfur fuel to attain environmental standard by 1978[4)]

	Overpopulated area	Polluted area	Precaution area	Prevention area
1967				
Amount(10,000kl)	2,297	1,307	-	3,064
Average sulfur content (%)	2.41	2.51	-	2.45
Pollution(SO_2 ppm)	0.38	0.24	-	-

1973				
Amount(10,000kl)	4,360	2,830	2,750	9,940
Average sulfur content (%)	0.90	1.30	1.45	1.20
Pollution(SO_2 ppm)	0.27	0.20	0.20	-
1978				
Amount(10,000kl)	5,500	4,600	5,400	15,500
Average sulfur content (%)	0.55	0.80	1.00	0.80
Pollution(SO_2 ppm)	0.20	0.20	0.20	-

1. The environmental standard requires that SO_2 concentration should be below 0.2ppm for more than 99% of total hours (1.6).

2. Fuel includes crude oil for fuel, LNG, etc.

3. Effect of desulfurization is included in the sulfur content.

Judging from the crude oil import situation not much low-sulfur oil can be expected. To attain the SO_2 level indicated in the table, 43.4 million kiloliters (275 million barrels) of heavy oil has to be subjected to hydrodesulfurization to decrease the sulfur content to 1.35% on the average in addition to flue-gas desulfurization of 1.7 million kiloliters in 1973 (Table 1.10).

Table 1.10 1973 target sulfur content in fuel and means of achieving target[4]

	Amount(1,000kl)	Average sulfur content(%)
Heavy oil		
Low-sulfur	27,500	0.55
Medium-sulfur	51,800	2.35
High-sulfur	19,800	3.75
Residual hydrodesulfurization	43,400	1.35
Flue-gas desulfurization	1,700	0.75
Import of heavy oil		
Class C, including crude oil for fuel	30,200	1.00
Class A	2,000	1.50
Imported LNG	1,400	
Total for fuel	177,800	1.70

1.6 Environmental standard

The environmental standard for SO_2 has been set out as follows:

1) The hourly average SO_2 concentration should not exceed 0.2ppm in not less than 99% of the total number of hours in a given year.
2) The daily average SO_2 concentration should not exceed 0.05ppm in not less than 70% of the total number of days in a given year.
3) The hourly average SO_2 concentration should not exceed 0.05ppm in not less than 88% of the total number of hours in a given year.
4) The yearly average of hourly concentrations should not exceed 0.05ppm.

The yearly averages in the most polluted districts in major cities are shown in Table 1.11. In many of the districts, SO_2 concentration still exceeds the standard although the concentration in 1970 is lower than in 1969.

Table 1.11 Yearly average concentration of SO_2

	1967	1968	1969	1970
Sapporo	0.040	0.040	0.049	0.049
Tokyo	0.074	0.080	0.085	0.065
Yokohama	0.064	0.060	0.060	0.058
Kawasaki	0.10	0.084	0.075	0.062
Nagoya	0.051	0.054	0.056	0.052
Yokkaichi	0.081	0.052	0.051	0.045
Kyoto	0.053	0.057	0.053	0.052
Osaka	0.091	0.082	0.095	0.090
Kobe	0.038	0.051	0.049	0.048
Omuta	0.052	0.055	0.057	0.052

1.7 Emission standard

The emission standard is given by the following equation:

$$q = k \times 10^{-3} He^2$$

q: amount of sulfur oxide, Nm^3/hr

k: the value shown in Table 1.12

He: effective height of stack (meters)

Table 1.12 The values of k

Rank	k	Districts
1	11.7	Tokyo, Osaka, Yokkaichi, etc.
2	12.8	Kashima, Chiba, Kurashiki, etc.
3	14.0	Muroran, Nagoya, Himeji, etc.
4	15.8	Sapporo, Kyoto, Hatogaya, etc.
5	17.5	Hitachi, Niihama, Omuta, etc.
6	20.4	Niigata, Onoda, Ube, etc.
7	23.3	Kure, Tokuyama, Wanyo, etc.
8	26.3	Hachinoe, Kamaishi, Nobeoka, etc.

A special k value 5.26 has been applied recently to areas which are already heavily polluted such as the city areas of Tokyo and Osaka, and industrial areas such as Yokkaichi and Kawasaki. Electric power plants have built tall stacks as high as 200 meters in an effort to meet the emission standard.

In addition to these national standards, there are regulations on sulfur content of oil enforced in specific areas. For example, an ordinance issued by the Governor of Tokyo is shown in Table 1.13.

Table 1.13 Ordinance on sulfur content of fuel oil (Tokyo)

	Plants		Buildings	
	Consumption of oil (liter/day)	Maximum S (%)	Consumption of oil (liter/day)	Maximum S (%)
City area	1,000 to 4,000	1.3 (1.5)*	300 to 10,000	1.0 (1.3)*
	4,000 to 10,000	1.0 (1.3)	over 10,000	0.5(1.0)
	over 10,000	0.5 (1.3)		
Other areas	1,000 to 10,000	1.3 (1.7)	300 to 10,000	1.0 (1.3)
	over 10,000	1.0 (1.3)	over 10,000	0.5 (1.0)

* Parenthesized figures are for existing plants and buildings. Other figures are for those to be newly built.

As public opinion on air pollution is becoming more and more critical, both the k values and the SO_2 concentration in the environmental standard are to be reduced by about 40%. By this change the sulfur abatement policy would be revised to require larger amounts of imported low-sulfur fuels, more desulfurization, and higher stacks.

2 Outline of recent developments in desulfurization

2.1 Hydrodesulfurization of heavy oil

Many hydrodesulfurization plants have been built since 1967 in various districts of Japan (Table 2.1). Three of them use the topped-crude desulfurization process (or the atmospheric residual desulfurization process which is often referred to as the direct process) and others the vacuum gas-oil desulfurization process (indirect process). By the direct process, up to about 75% of sulfur in oil can be removed (Figure 2.1) but the life of catalyst is a big problem.

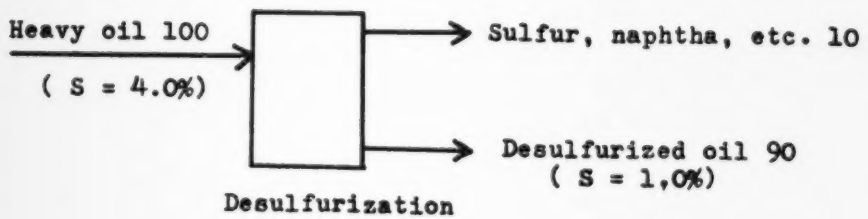


Figure 2.1 Rough material balance in topped-crude hydrodesulfurization (direct process)

By the indirect process, heavy oil is first distilled under vacuum. The distillate is desulfurized down to 0.2% sulfur without any significant technical trouble (Figure 2.2). The desulfurized oil is normally mixed with the residue of the vacuum distillation to be used as fuel oil. The product contains 2.4% sulfur when heavy oil with 4.0% sulfur is treated. Therefore, the removal is not satisfactory to meet the severe requirements for SO_2 control.

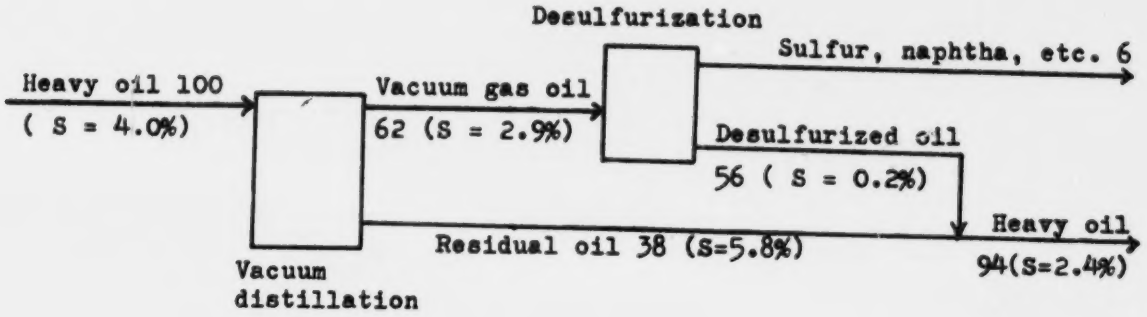


Figure 2.2 Rough material balance in vacuum gas-oil hydrodesulfurization (indirect process)

Table 2.1 Hydrodesulfurization plants in Japan

Refiner	Plant site	Process	Completed	Capacity(per day) Oil(BPSD)	Capacity(per day) Sulfur(tons)
Idemitsu Kosan	Chiba	UOP (T)*	1967	40,000	240
Fuji Oil	Sodegaura	CRC(V)**	1968	23,000	90
Toa Nenryo	Wakayama	ERE(V)	1968	25,000	162
Daikyo Oil	Umaokoshi	Gulf (V)	1969	17,500	100
Nippon Oil	Negishi	CRC (V)	1969	40,000	173
Showa Oil	Kawasaki	Shell (V)	1969	16,000	60
Kyushu Oil	Oita	Shell (V)	1969	14,000	50
Mitsubishi Oil	Mizushima	UOP (V)	1969	30,000	90
Maruzen Oil	Chiba	Union(V)	1969	35,000	150
Seibu Oil	Yamaguchi	Shell (V)	1969	4,000	25
Nippon Mining	Mizushima	Gulf (V)	1970	27,760	150
Koa Oil	Marifu	CRC (V)	1970	8,000	35

General Oil	Sakai	ERE (V)	1970	31,000	66
Kashima Oil	Kashima	UOP (T)	1970	45,000	240
Idemitsu Kosan	Himeji	UOP (T)	1970	40,000	200
Daikyo Oil	Umaokoshi	Gulf (V)	1970	17,500	70
Kansai Oil	Sakai	ERE (V)	1971	20,000	80
Koa Oil	Osaka	CRC (V)	1971	12,000	50
Toa Nenryo	Kawasaki	ERE (V)	1971	51,000	200
Subtotal				496,260	2,231
Nippon Oil	Negishi	CRC (V)	1972	28,000	
Idemitsu Kosan	Himeji	Gulf (T)	1972	40,000	
Kyokuto Petroleum	Chiba	UOP (V)	1972	60,000	
Kashima Oil	Kashima	(V)	1972	11,000	
Asia Oil	Sakaide	(V)	1972	50,000	
Nippon Oil	Muroran	CRC (V)	1973	40,000	
Toa Oil	Nagoya	(V)	1973	30,000	
Subtotal				259,000	
Total				755,260	

* Topped-crude desulfurization (direct process)

** Vacuum gas-oil desulfurization (indirect process)

2.2 Waste-gas desulfurization

Large-scale desulfurization plants are listed in Table 2.2. The plants No. 1 through No. 6 are commercial plants designed to produce sodium sulfite solutions for paper industry. Others produce sulfuric acid, gypsum,

Table 2.2 Major plants for waste-gas desulfurization

No.	Developer	User	Plant site	Absorbent	Product	Gas treated 1,000Nm^3/hr	Completion
1	Kureha Chemical	Kureha Chemical	Nishiki	NaOH	Na_2SO_3	600[a]	1968
2	Oji Paper	Oji Paper	Kasugai	NaOH	Na_2SO_3	800[a,b]	1969-1971
3	Showa Denko	Showa Denko	Kawasaki	NaOH	Na_2SO_3	150[a]	1970
4	Showa Denko	Ajinomoto	Kawasaki	NaOH	Na_2SO_3	270[a]	1971
5	Showa Denko	Nippon Phosphoric	Sodegaura	NaOH	Na_2SO_3	80[c]	1971
6	Bahco-Tsukishima	Daishowa	Yoshinaga	NaOH	Na_2SO_3	335[b]	1971
7	Wellman-Lord	Nihon Synthetic Rubber	Chiba	Na_2SO_3	$SO_2(H_2SO_4)$	200[a]	1971
8	Wellman-Lord	Toa Nenryo	Kawasaki	Na_2SO_3	SO_2	60[d]	1971
9	Mitsubishi H.I.	Nippon Kokan	Koyasu	$Ca(OH)_2$	gypsum	60[c]	1968
10	Mitsubishi H.I.	Kansai Electric	Amagasaki	$Ca(OH)_2$	gypsum	100[a]	1972
11	Japan Eng. Co.	Tomakomai Chem.	Tomakomai	$Ca(OH)_2$	gypsum	52[e]	1972
12	Sumitomo	Kansai Electric	Sakai	Carbon	$SO_2(H_2SO_4)$	175[a]	1971
13	Mitsubishi H.I.	Chubu Electric	Yokkaichi	MnO_x	$(NH_4)_2SO_4$	326[a]	1972
14	Hitachi Ltd.	Tokyo Electric	Kashima	Carbon	H_2SO_4(gypsum)	420[a]	1972
15	Jinkoshi	Nippon Kokan	Keihin	NH_4OH	$(NH_4)SO_4$	150[e]	1972
16	Chiyoda C.E.	Nippon Mining	Mizushima	dil. H_2SO_4	gypsum	70[d]	1972
17	Chemico	Mitsui Aluminum	Omuta	$Ca(OH)_2$	$CaSO_3$	512[f]	1972
18	Shell	Showa Yokkaichi Sekiyu	Yokkaichi	CuO	SO_2	120[a]	1973

a: Oil-burning boiler b: Kraft recovery boiler c: Sulfuric acid plant
d: Claus furnace e: Sintering plant f: Coal-burning boiler

ammonium sulfate, etc. In Japan, it is necessary to obtain usable by-products by desulfurization because there is not enough land for waste disposal. Several other processes are being tested on a smaller scale as will be described later.

2.3 Government policy for development of desulfurization technology

National research projects for desulfurization

The Agency of Industrial Science and Technology, MITI, has set forth the following guideline for desulfurizati n: Large electric power plants should perform flue-gas desulfurization by which more than 80% of SO_2 can be removed. Other consumers of heavy oil, such as various plants and buildings, should use low-sulfur oil obtained by direct hydrodesulfurization. Based on this guideline, the Agency has awarded contracts to several groups for the development of processes for flue-gas desulfurization and heavy-oil desulfurization (Topped-crude hydrodesulfurization) as shown in Tables 2.3 and 2.4.

Table 2.3 Development of desulfurization processes under contract of Agency of Industrial Science and Technology

	Flue-gas desulfurization		Topped-crude hydrodesulfurization	
Year	Mitsubishi (manganese)	Hitachi (carbon)		
1966	Pilot plant	Pilot plant	Research on catalyst	
1967				
1968	Prototype plant	Prototype plant		Pilot plant
1969				
1970				
1971				

Table 2.4 Expenditures of the Agency of Industrial Science and Technology for the contracts(millions of yen)

Year	Flue-gas desulfurization	Topped-crude hydrodesulfurization	Total
1966	325	0	325
1967	455	100	555
1968	547	240	787
1969	45	428	473
1970	0	305	305
1971	0	163	163

(1) Contracts for flue-gas desulfurization

Contracts were awarded to Mitsubishi Heavy Industries (active manganese process, DAP-Mn process) for the period 1966 through 1968 and also to Hitachi Ltd. (activated carbon process) for 1966 through 1969 to build pilot plants followed by prototype plants. Each prototype plant was capable of treating 150,000Nm^3/hr gas from oil-fired power plants(50MW equivalent).

(2) Contracts for topped-crude hydrodesulfurization

A contract was awarded to a research group of ten oil refiners for the 1967-1969 period to develop a catalist for desulfurization. Under another contract for 1969 through 1971 a new suspended-bed reactor with a capacity of 500BPSD has been built and tested by Nippon Oil.

Researches on desulfurization have been made also by institutes which belong to the Agency. Government Research Institute, Tokyo, is working on hydrodesulfurization. National Research Institute of Pollution and Resources (former Resources Research Institute) has been working on flue-gas desulfurization by the sodium carbonate process and also on catalysts for hydrodesulfurization.

Under the contracts, all expenses for development are supplied by the Government. After completion of the tests under contract, each organization makes further development at their own expense.

Projected new system for the development of pollution control technology

MITI plans to set up a new program for the development of "closed systems" which cause no emission of pollutants, and is trying to get budget allocations for the program. Under this program MITI has tentatively selected three projects for important closed systems deemed worth developing. The three are as follows:

(1) Gasification desulfurization (Ube process, which will be described in 3.6). (2) Production of caustic soda by electrolysis without using mercury. (3) Production of pulp and paper without giving any troublesome muddy material.

Each of the projects is expected to require 1 to 2 billion yen to build prototype test plants. MITI is to supply 75% of the total expense subject to budget appropriations.

3 Desulfurization of heavy oil

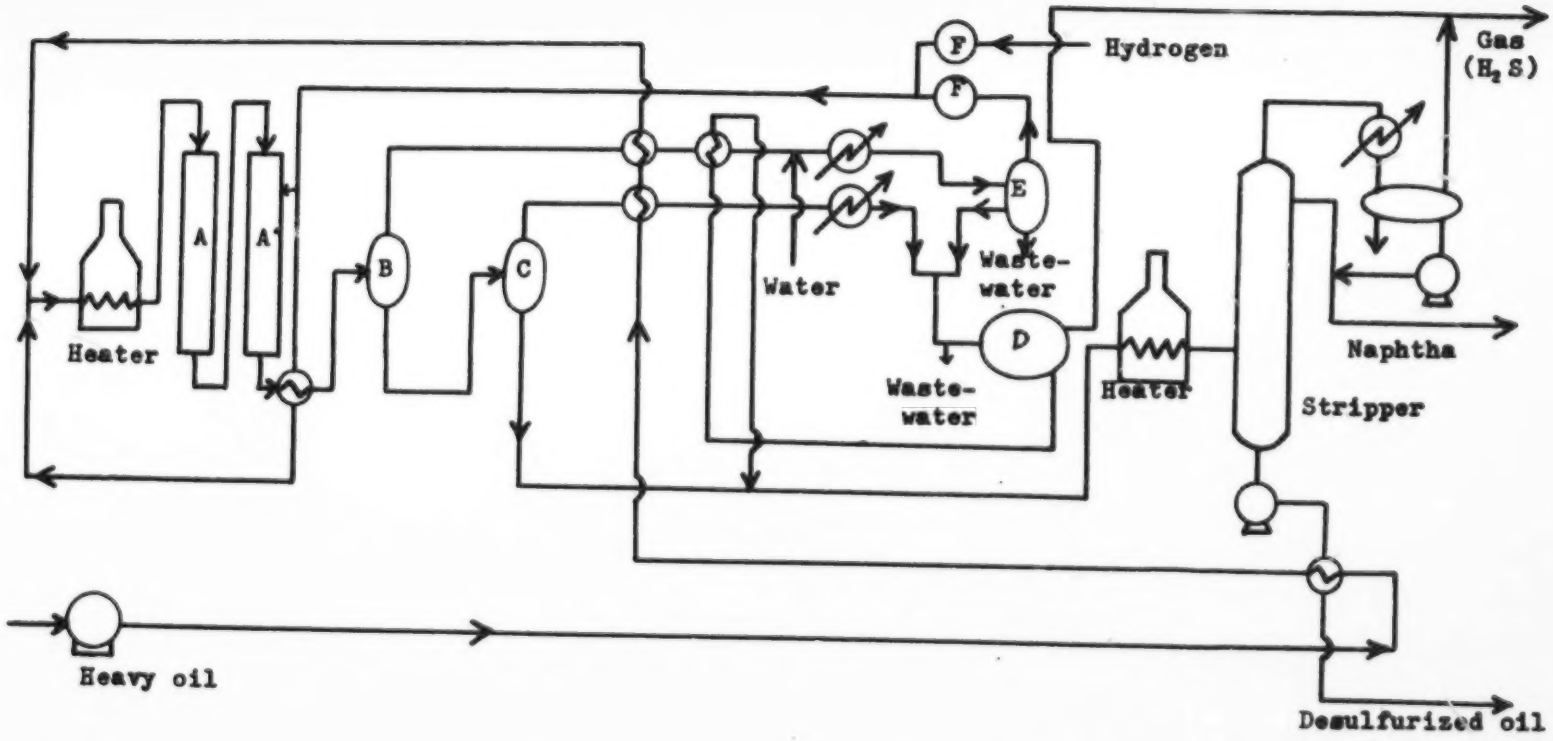
3.1 UOP-RCD Isomax process for topped-crude hydrodesulfurization

Description Two commercial-scale plants using the UOP-RCD process are in operation--one at Chiba and the other at Kashima (Table 2.1) The Chiba plant, owned by Idemitsu Kosan, was completed in 1967 as the first commercial plant in the world for topped-crude desulfurization. The Kashima plant was completed in 1970.

The flow sheet of the process is shown in Figure 3.1. Heavy oil is preheated, mixed with hydrogen, reheated, and charged into the two reactors in series. The reactors contain molybdenum-cobalt catalyst in fixed beds. The reaction is carried out at 380 to 430°C temperature under 140 to 160kg/cm^2 pressure. The liquid hourly space velocity (LHSV) is maintained at about 1. The discharge from the reactors is sent to the hot separator where hydrogen-rich gas is separated from liquid. The liquid is sent to the flash drum and then to the stripper. Desulfurized oil is discharged from the bottom of the stripper while naphtha and hydrogen sulfide are discharged from the top.

The gas from the hot separator is sent to the cold separator where hydrogen is separated and recycled to the reactor. The remainder from the separator is sent to the cold flash drum where some hydrogen sulfide is released. Hydrogen sulfide from both the flash drum and the stripper is sent to a Claus furnace to be converted into sulfur.

Operation data The first plan at Chiba had mechanical troubles for over a year since operation was started in 1967. The troubles have been overcome, and satisfactory operation has been carried out recently. The plant at Kashima has been working well since operation was started in 1970. Typical operation data for the Chiba plant are shown in Table 3.1. The average consumption of hydrogen is 500 to 600 SCF per barrel of heavy oil charged.



A, A' : Reactors B : Hot separator C : Hot flash drum
D : Cold flash drum E : Cold separator F : Compressor

Figure 3.1 Flow sheet of UOP (RCD) Isomax process

Table 3.1 Typical operation data

		BPSD	Ratio to charge	Sulfur (% in oil)
Charge	heavy oil	40,075	100	3.94
	gasoline	362	0.9	-
Product	gas oil	2,460	6.1	0.04
	desulfurized oil	37,500	96.3	1.01

Life of catalyst The catalyst is poisoned by heavy metals contained in heavy oil--by nickel and particularly by vanadium (Table 3.2).

Table 3.2 Viscosity and ingredients of heavy oil obtained by topping of various crudes

	Kuwait	Khafji	Iranian Light	Iranian Heavy	California
Viscosity (cSt, 50°C)	250	500	250	350	-
Sulfur (%)	3.8	4.1	2.5	2.6	1.9
Vanadium (ppm)	45	55	63	165	80
Nickel (ppm)	15	25	29	55	125

The heavy oil from Iranian Heavy (Gach Saran) crude contains the largest amount of vanadium and is most unfavorable for the catalyst. Catalyst life is about 25bbl/lb for Iranian Heavy and 35 to 45bbl/lb for other heavy oils.

Carbon deposits on the catalyst surface pose another problem. The deposits can be reduced by using a higher hydrogen pressure. They occur remarkably when the reaction temperature exceeds 430°C.

The catalyst used to be regenerated after several months' operation. The regeneration requires much sodium hydroxide. Recently a new type of cheaper RCD catalyst has been introduced which is abandoned without regeneration. Better economy is achieved in this way.

Investment and operation costs According to a recent estimation[5], investment cost for a plant to treat 50,000BPSD Khafji heavy oil and requirements for operation are as follows:

(Tables 3.4 and 3.5).

Table 3.4 Investment cost for desulfurization plant (millions of yen)

	Isomax (50,000BPSD)	Hydrogen production ($1.15 \times 10^6 Nm^3/day$)	Sulfur recovery (225t/day)	Total
Equipment	4,800	1,300	491	6,591
Patent	1,065	206	-	1,271
Catalyst	830	155	20	1,005
Chemicals	-	14	10	24
Technical guidance	25	7	5	37
Total	6,720	1,682	526	8,928

Table 3.5 Requirements for operation of 50,000BPSD plant

	Isomax plant	Hydrogen plant	Sulfur plant	Total
Electric power (kW)	2,370	1,600	510	4,480
Steam (tons/hr)	2.5	-1.1	26.6	28
Water for boilers (tons/hr)	4.0	73	-26.6	50.4
Process water (tons/hr)	30	33	-	63
Cooling water (tons/hr)	4,030	100	1,300	5,430
Fuel (10^6kcal/hr)	88	92	2.0	100.4
Catalyst (Isomax) (kg/day)	650	-	-	650
Catalyst (hydrogen) (¥10^3/day)	-	165	-	165
Other chemicals (kg/day)	-	61	310	371

Operation cost, according to Idemitsu, is about ¥2,100 to treat one kiloliter of Khafji heavy oil to decrease sulfur content from 4 to 1%. Another estimate[5] gives a nearly equal cost (6.2). One report places the operation cost at as low as ¥1,155[6]. This estimation seems too low. It is possible, however, for the cost to be reduced to a little less than ¥2,000 through future improvement of catalyst if the by-product sulfur can be sold at a reasonable price.

3.2 Gulf process for topped-crude hydrodesulfurization[7)]

State of development A commercial plant capable of treating 25,000BPSD heavy oil has been in operation since 1970 at the Mizushima works of Nippon Mining Co. Another plant, with a 40,000BPSD capacity, is to be built in 1972 at the Himeji works, Idemitsu Kosan.

Description The flow sheet of the process is given in Figure 3.2. The process is similar to the UOP-RCD process (3.1), but differs from the latter in that:

(1) Two reactors are provided in parallel; either one or both of them can be used.
(2) Gas from the separator is washed in a scrubber by amine to remove hydrogen sulfide; thus, hydrogen gas without hydrogen sulfide is recycled resulting in better desulfurization.
(3) A portion of the cold hydrogen gas from the scrubber is introduced into the reactors for cooling to maintain an optimum reaction temperature--300 to 350°C--whereas in the early UOP-RCD process cold oil was recycled for cooling.
(4) A molybdenum-nickel-cobalt catalyst is used which is fairly cheap and is abandoned after about 6 months' use without being regenerated.

Operation data The Mizushima plant has been in satisfactory operation since it was started in 1970. Typical operation data using Kuwait heavy oil (sulfur 3.98%, vanadium 52ppm, nickel 15ppm) are shown in Table 3.6.

Table 3.6 Products from desulfurization of Kuwait heavy oil (130 to 140kg/cm^2 pressure, 320 to 330°C temperature, LHSV nearly 1)

Products (% by volume)			
$C \sim C_4$	$C_5 \sim 343°C$	Desulfurized heavy oil	Sulfur content of desulfurized heavy oil (%)
0.6	4.8	96.3	0.98

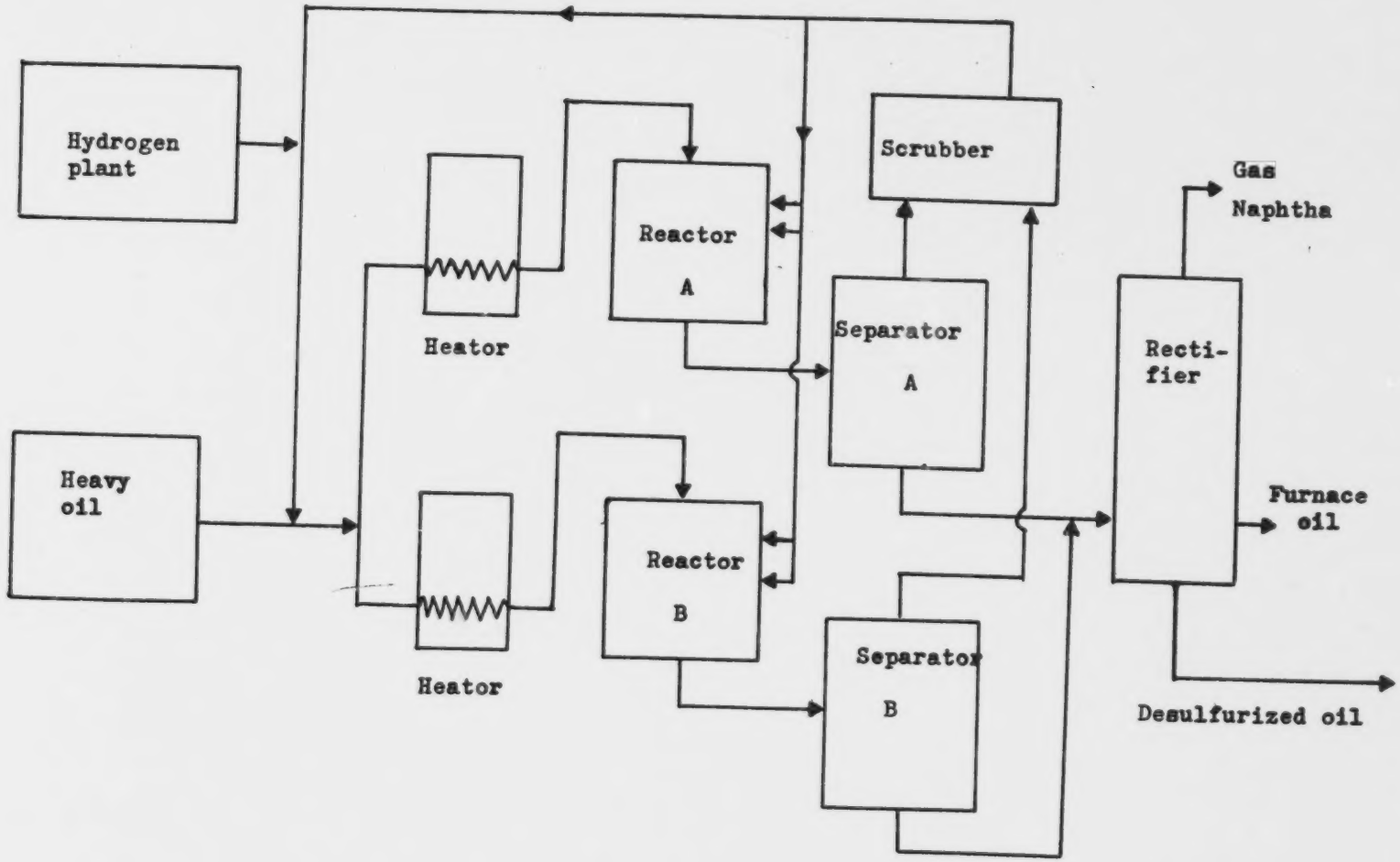


Figure 3.2 Flow sheet of Gulf process

To maintain a high desulfurization rate, the reaction temperature is gradually raised as the catalyst activity is lowered during operation (Figure 3.3). The catalyst is ruined at temperatures above 400°C. The plant was designed for a catalyst change every 6 months.

Khafji heavy oil also can be desulfurized by the plant although treatment is a little harder than with Kuwait heavy oil. To desulfurize Iranian Heavy (Gach Saran) oil which is rich in vanadium, it is required to change the plant design.

Economics Total investment cost for a desulfurization plant capable of treating 40,000BPSD of Kuwait heavy oil to reduce sulfur to as low as 1% is estimated at about ¥8 billion including the hydrogen plant and sulfur recovery plant. The operation cost would be ¥2,200 to 2,700 per kiloliter of oil neglecting by-product credit from selling the recovered sulfur.

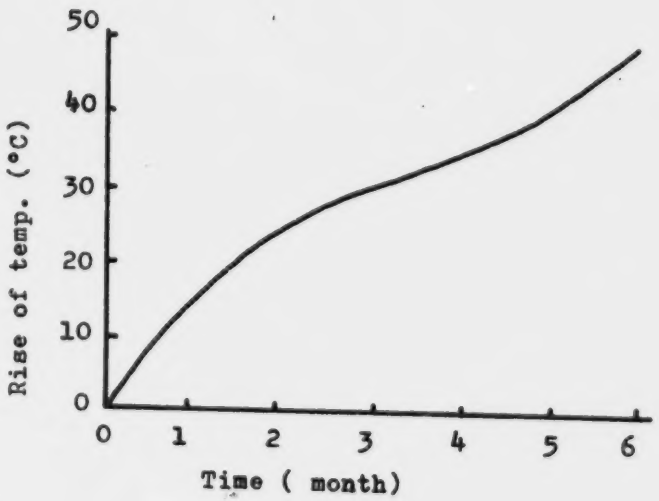


Figure 3.3 Rise of temperature during operation

3.3 MDS process for topped-crude hydrodesulfurization[8)]

Developer Government Chemical Research Institute, Tokyo
1-1-5, Honmachi, Shibuya-ku, Tokyo

State of Development A pilot plant using a reactor 200mm in diameter is in successful operation. A much larger pilot plant is planned.

Description This process is characterized by the use of a moving-bed reactor. A device enables the catalyst to be renewed continuously without having to stop plant operation. A model of the reactor is shown in Figure 3.4.

The catalyst, charged from the top, gradually descends through the reactor without being fluidized. A mixture of heavy oil and hydrogen is charged from the bottom and comes in contact with the old catalyst first. Impurity in oil is filtered away by the old catalyst; this obviates the use of a filter which is needed with other types of reactors. Catalyst in the upper layer is always kept clean and maintains high reactivity. A flow sheet of the system is shown in Figure 3.5. Typical operation data are given in Tables 3.7 and 3.8.

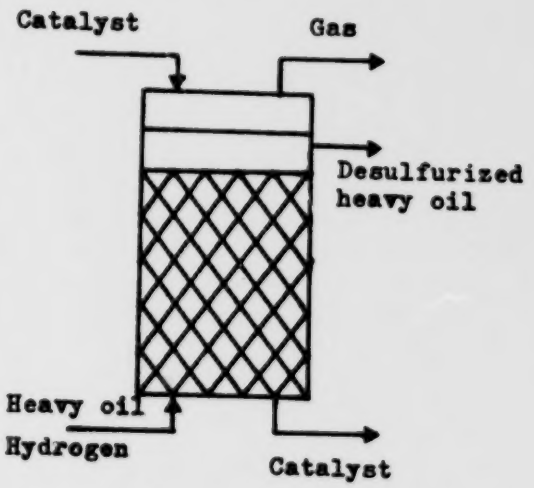
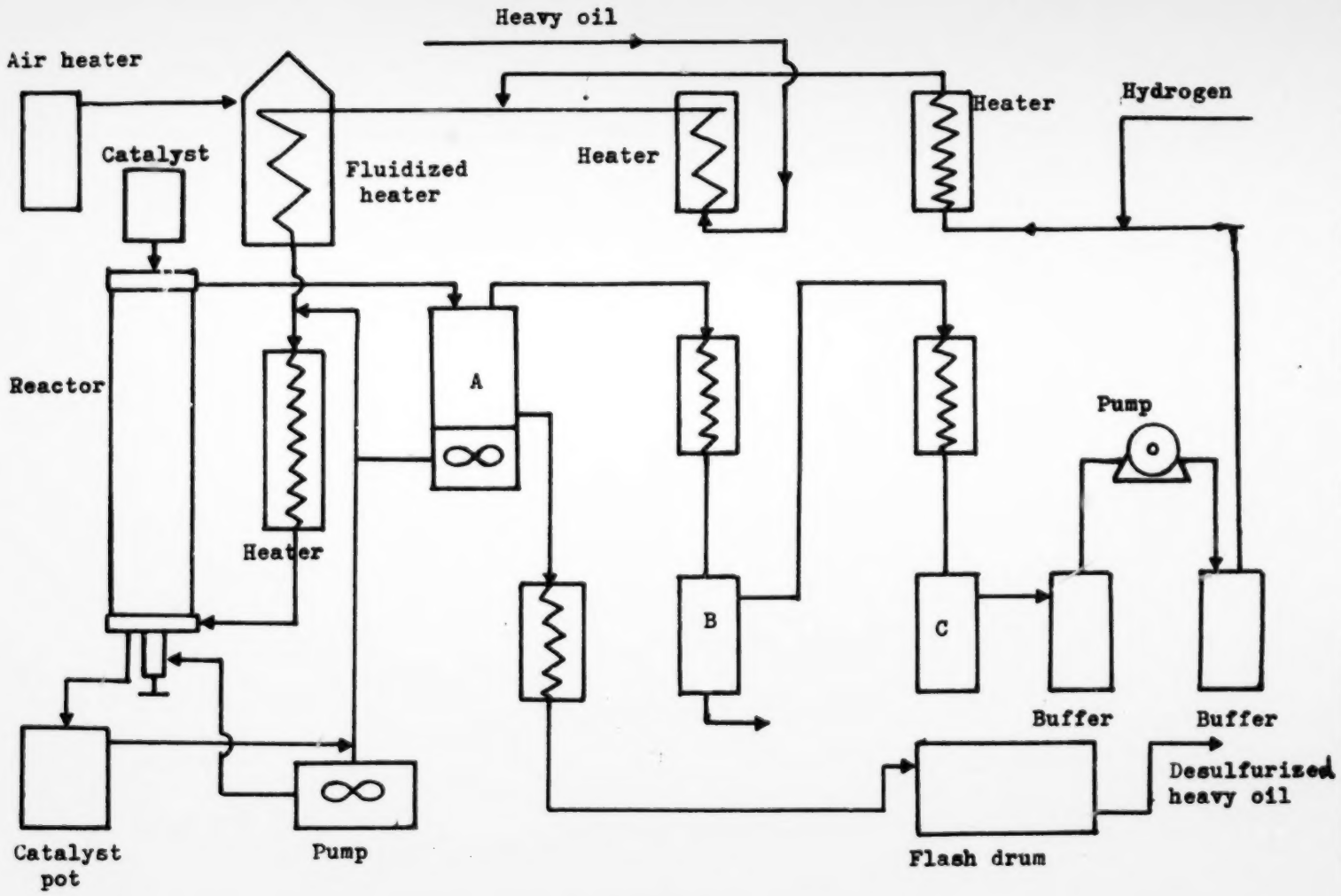


Figure 3.4 Model of moving bed reactor

Advantages The catalyst is renewed continuously during plant operation, whereas in the UOP and Gulf processes, which use a fixed-bed reactor, plant operation has to be stopped to change the catalyst. Reaction efficiency is better with the moving bed than with an ebullated bed.



A : Hot separator B : Cold separator C : Scrubber

Figure 3.5 Flow sheet of MDS process with a pilot reactor 200 mm in diameter

Table 3.7 Typical operation data (Khafji heavy oil)

	C-2	F-2	G-3
Pressure (kg/cm^2)	200	200	200
Temperature of catalyst			
Maximum (°C)	403	392	403
Minimum (°C)	367	381	393
Average (°C)	385	387	398
LHSV (hr^{-1})	1.01	1.27	0.62
Oil recycle ratio	1.36	1.68	6.47
Sulfur in heavy oil (%)	4.11	4.30	4.30
Sulfur removal (%)	81.9	76.4	90.6
Hydrogen consumption(Chem. Nm^3/kl)	177	149	186
Sulfur in desulfurized oil (%)	0.76	1.07	0.67
Viscosity of desulfurized oil (Cst at 50°C)	93.6	148.2	58.7
Distillation test			
I. B. P. (°C)	204	163	138
5% (°C)	283	307	225
10% (°C)	306	328	280
300°C + (vol.%)	91.5	96.1	83.5

Table 3.8 Material balance in Khafji heavy oil tests (kg/hr)

	C-2	F-2	G-3
Heavy oil charged	86.50	104.20	51.21
Hydrogen charged	1.81	1.73	1.01
Total	88.31	105.93	52.22
Desulfurized heavy oil	84.91	101.40	44.99
Hydrogen released	0.46	0.40	0.14
Hydrogen sulfide	3.09	3.40	1.99
$C_1 \sim C_4$	0.26	0.27	0.42
Total	88.75	105.47	47.54

3.4 Other tests on topped-crude hydrodesulfurization

(1) Suspending-bed hydrodesulfurization

Developer The Agency of Industrial Science and Technology with Nippon Oil Co., partly with Chiyoda Chemical Engineering Co. and Niigata Engineering Co.

Description Pilot plant tests on suspending-bed hydrodesulfurization have been carried out since 1969 using a cobalt-molybdenum catalyst. In preliminary tests with a reactor 200mm in diameter, sulfur removal reached 75 to 80% with Khafji heavy oil by reaction at 380 to 390°C under 195kg/cm^2 pressure at LHSV 1.0 to 1.5.

Tests with a larger reactor to treat 250BPSD have been carried out since 1970. A modified reactor with the same capacity was completed recently. Details of these tests have not yet been made known.

(2) Tests on catalyst

The National Research Institute of Pollution and Resources has worked on improvement of a cobalt-molybdenum catalyst using alumina and silica-alumina as carriers. After screening tests, 1,000 to 2,000 hours' tests were made on the selected catalyst. Over 80% sulfur removal was attained with the catalyst.

A research group of ten oil refiners has worked on nickel-molybdenum-alumina catalysts. A good catalyst was obtained after 1,000 to 1,500 hours' tests. By cooperation with the National Institute of Pollution and Resources, 2,000 to 3,000 hours' life tests have been made.

Details of these tests have not been published yet except a fundamental study of the catalytic reactions involved.[9]

3.5 Vacuum gas-oil hydrodesulfurization

Description Sixteen commercial plants for vacuum gas-oil hydrodesulfurization are in operation and several others are under construction (Table 2.1). Typical examples of material balance and flow sheet of the process are shown in Figure 3.6 and Figure 3.7.

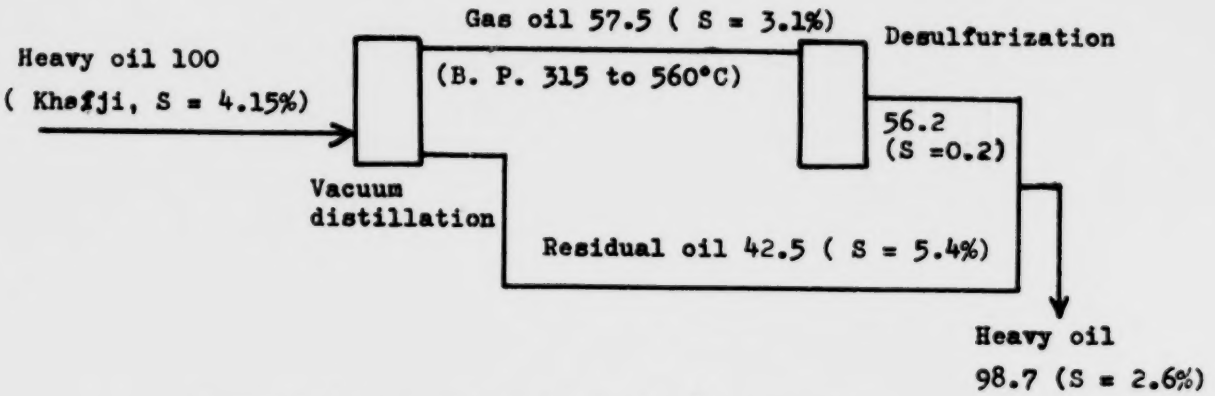
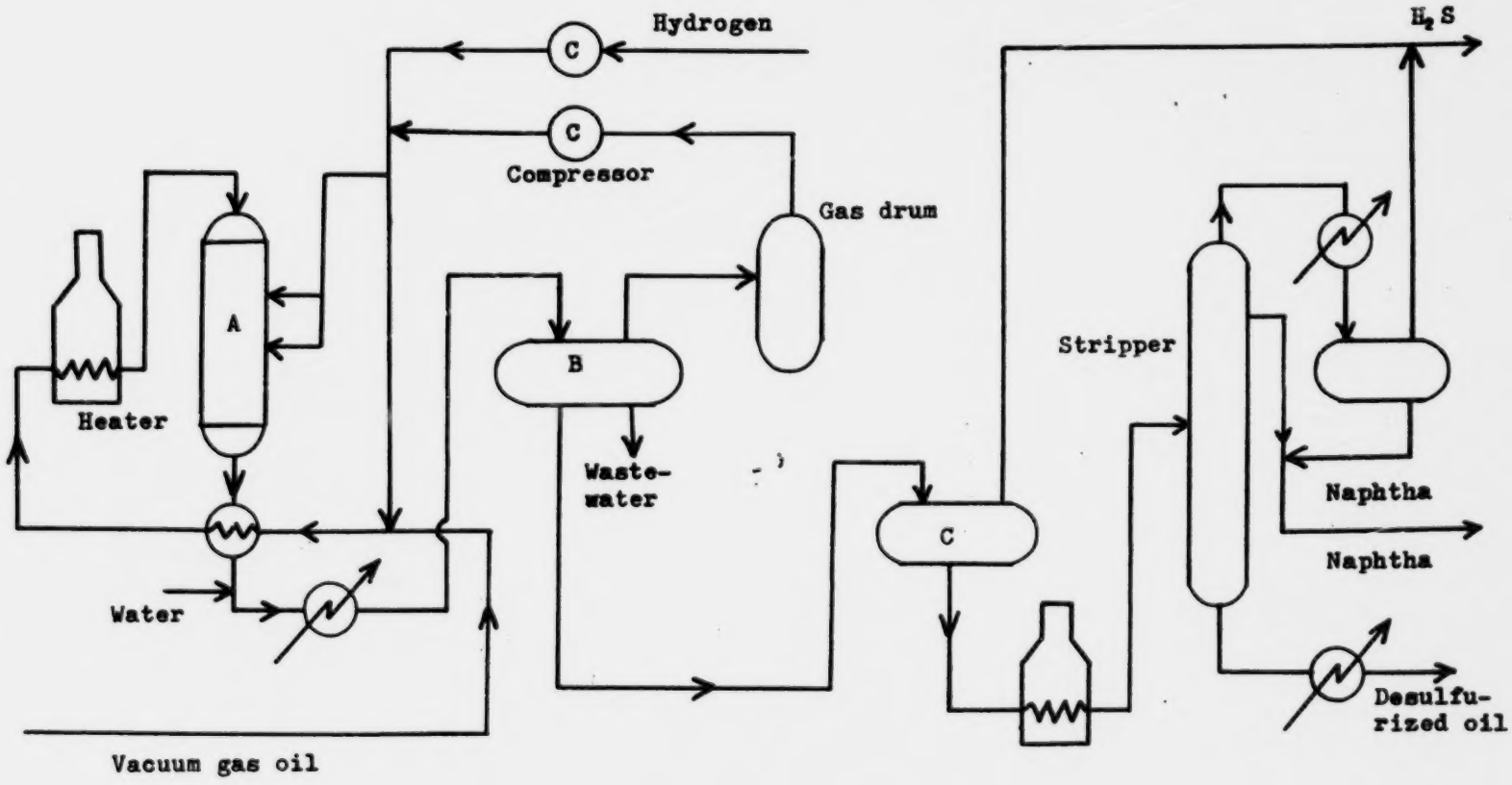


Figure 3.6 Material balance in VGO process

Vacuum gas oil (gas oil) obtained by vacuum distillation of heavy oil, with a boiling point between 300 and 560°C and with essentially no vanadium or nickel is subjected to hydrodesulfurization under the conditions indicated in Table 3.9.

Table 3.9 Condition of VGO desulfurization as compared with TC desulfurization

	Vacuum gas-oil desulfurization	Topped-crude desulfurization
Oil charged	Vacuum gas oil	Heavy oil
Reaction temperature (°C)	Below 450	Below 450
Reaction pressure (kg/cm^2)	90 to 110	130 to 160
LHSV	2.0 to 3.0	0.5 to 1.0
Catalyst life (years)	3 to 5	0.5 to 1
Hydrogen consumption (SCF/bbl)	300 to 400	500 to 800



A : Reactor B : High pressure separator C : Low pressure separator

Figure 3.7 Flow sheet of VGO hydrodesulfurization process

The desulfurization is carried out far more easily than with the topped-crude process. The catalyst life is as long as 5 years. Sulfur content of oil can be lowered to 0.2%. A typical example of the yield and properties of products is illustrated in Table 3.10.

Table 3.10 Yield and properties of products of VGO desulfurization

	Vol. %	Wt. %	Sulfur %	Viscosity(Cst, 50°C)
Charge				
Khafji VGO	100.0	100.0	3.2	33.0
Hydrogen	479	0.79		
Products				
H_2S		3.21		
$C_1 \sim C_5$		1.07		
$C_6 \sim 350°F$	1.84	1.50	0.005	
$350 \sim 600°F$	6.53	6.00	0.05	1.7
$600°F \sim$	92.07	89.01	0.20	33.0

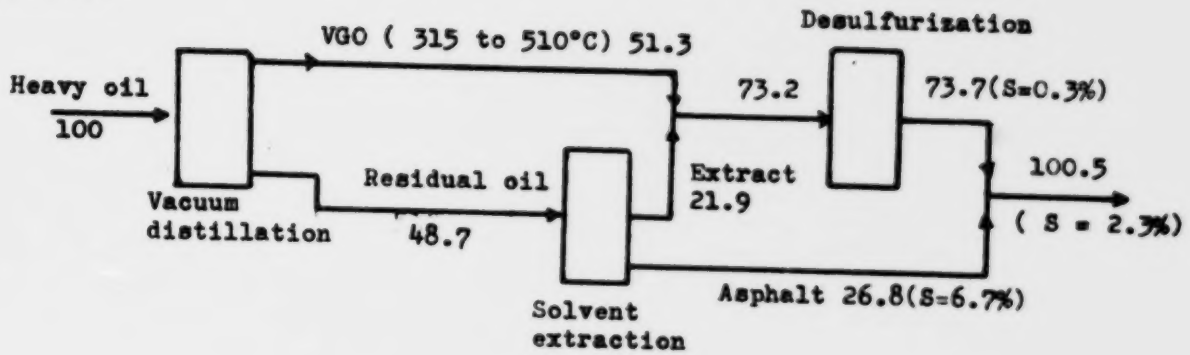
Advantages Operation is easy and well-established. Vacuum gas oil can be desulfurized to a very low sulfur content at a fairly low cost (6.2).

Desadvantages Utilization of the residual oil from vacuum distillation is a difficult problem. The oil, containing much sulfur, heavy metals and asphalt, is quite difficult to desulfurize. It is usually mixed with the desulfurized oil to be used as fuel oil (Figure 3.6). Overall desulfurization is poor in this case.

Modified process To obtain fuel oil with a lower sulfur content, a modified process as illustrated in Figure 3.8 is also used. In this process, the residual oil from vacuum distillation is extracted with a solvent such as propane, buthane or pentane. The extract is desulfurized together with the vacuum gas oil. More than a half of the sulfur in heavy oil can be removed in this way.

Another way to use the residual oil is to burn it as fuel and remove SO_2 from the flue gas. This process seems promising if it is used on a suitable scale and in favorable locations for flue-gas desulfurization.

Case 1



Case 2

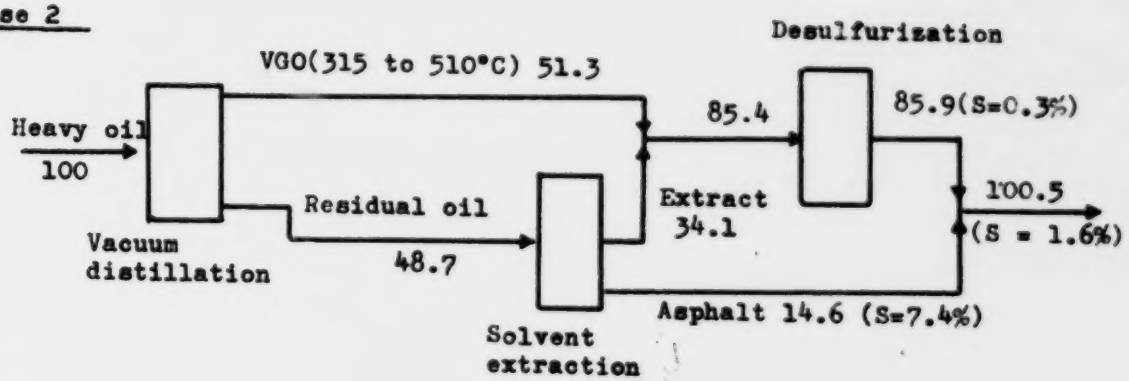


Figure 3.8 Modified VGO desulfurization processes
(Charge: Khafji heavy oil, S=4.15%. Hydrogen consumption: 450 SCF in case 1 and 550 SCF/bbl in case 2.)

3.6 Production of fuel gas by gasification desulfurization of heavy oil (Ube process)[10]

Developer Ube Industries Ltd.(2-1, Nagatacho, Chiyoda-ku, Tokyo)

State of development A pilot plant to treat 5 tons heavy oil per day is in operation. Construction of a prototype plant to supply the gas to a 40MW power plant has been decided recently. The total investment is estimated to be nearly ¥2 billion. The construction is scheduled to be completed by early 1973.

Outline Heavy oil is converted into fuel gas by partial oxidation with oxygen and steam. Sulfur is converted into hydrogen sulfide which is removed from the gas by the wet process. The flow sheet of the process is shown in Figure 3.9.

Description Heavy oil is charged into a fluidized reactor with oxygen and a jet stream of water vapor and undergoes partial oxidation at 800 to 900°C under atmospheric pressure. In the reactor, silica-alumina particles are fluidized to promote the gasification of heavy oil. The gas leaving the reactor is cooled to 450°C in a quencher by spraying residual oil from a distillator. The silica-alumina particles are fluidized also in the quencher and are gradually coated with tar. The tar-coated particles are continuously sent to a regenerator, where the tar is burned off by air.

The product gas from the quencher contains hydrogen, hydrocarbons, carbon oxides, hydrogen sulfide, and carbon. Carbon is removed by a cyclone. The gas then is cooled, condensed, and treated in a distillator. The distillate is cooled to separate gas oil and the gas is sent to an absorber, where hydrogen sulfide is removed to produce sulfur-free fuel gas. Part of the residual oil from the distillator is sent to the quencher and regenerator. The rest of the resudual oil is decomposed in a high-temperature reactor together with the carbon from the cyclone. The gas from the high-temperature reactor is also sent to the absorber.

The removal of hydrogen sulfide from the gas is carried out by the wet process, preferably by absorption with potassium carbonate. Hydrogen sulfide is regenerated from the solution in a discharger and sent to a Claus furnace to be converted into sulfur. The refined product gas contains about 19% H_2, 16% CH_4, 15% C_2H_4, 2% C_2H_6, 6% C_3H_6, 19% CO, and 17% CO_2 with essentially no sulfur. The heat of combustion of the product gas reaches about 8,000kcal/Nm^3.

The material balance is illustrated in Table 3.11. The production cost is estimated to be about ¥1,000/10^6kcal (Table 3.12) and thus the product

may be able to compete with imported LNG or low-sulfur oil (Figure 3.10). Better economy may be expected by using residual oil from vacuum distillation as illustrated in Figure 3.11.

Table 3.11 Material balance

Feedstock		Products	
Heavy oil	1,000	Refined dry gas	1,289
Oxygen	472	Steam	417
Steam	497	Gas oil	75
Total	1,969	Sulfur	35

Advantages

High-sulfur heavy oil and residual oil can be utilized.

Higher sulfur recovery than in hydrodesulfurization.

Far smaller desulfurization facilities than in flue-gas desulfurization because of the smaller amount of gas and higher concentration of sulfur compounds.

Disadvantages

Oxygen is required.

Separation of hydrogen sulfide from the gas containing olefins and carbon dioxide is not quite easy.

The whole system is not simple.

Table 3.12 Cost estimation

(Production of fuel gas to supply 500MW power plant.
Total capital cost is ¥6,840 million.)

	Case 1 (Operation 6,100 hours a year)		Case 2 (Operation 7,900 hours a year)	
	Annual cost (Millions of yen)	Cost (Yen/10^6kcal)	Annual cost (Millions of yen)	Cost (Yen/10^6kcal)
Heavy oil	4,038	613	5,230	613
Electricity	825	125	1,069	125
Cooling water	62	9	81	9
Reduction*	-462	-70	-599	-70
Depreciation**	684	104	684	80
Labor	80	12	80	9
Maintenance	205	31	205	24
Other fixed costs	358	55	358	42
Management	187	28	187	22
Interest	650	99	650	76
Total	6,627	1,006	7,945	930

* By sulfur and gas oil

** 10% of total investment cost

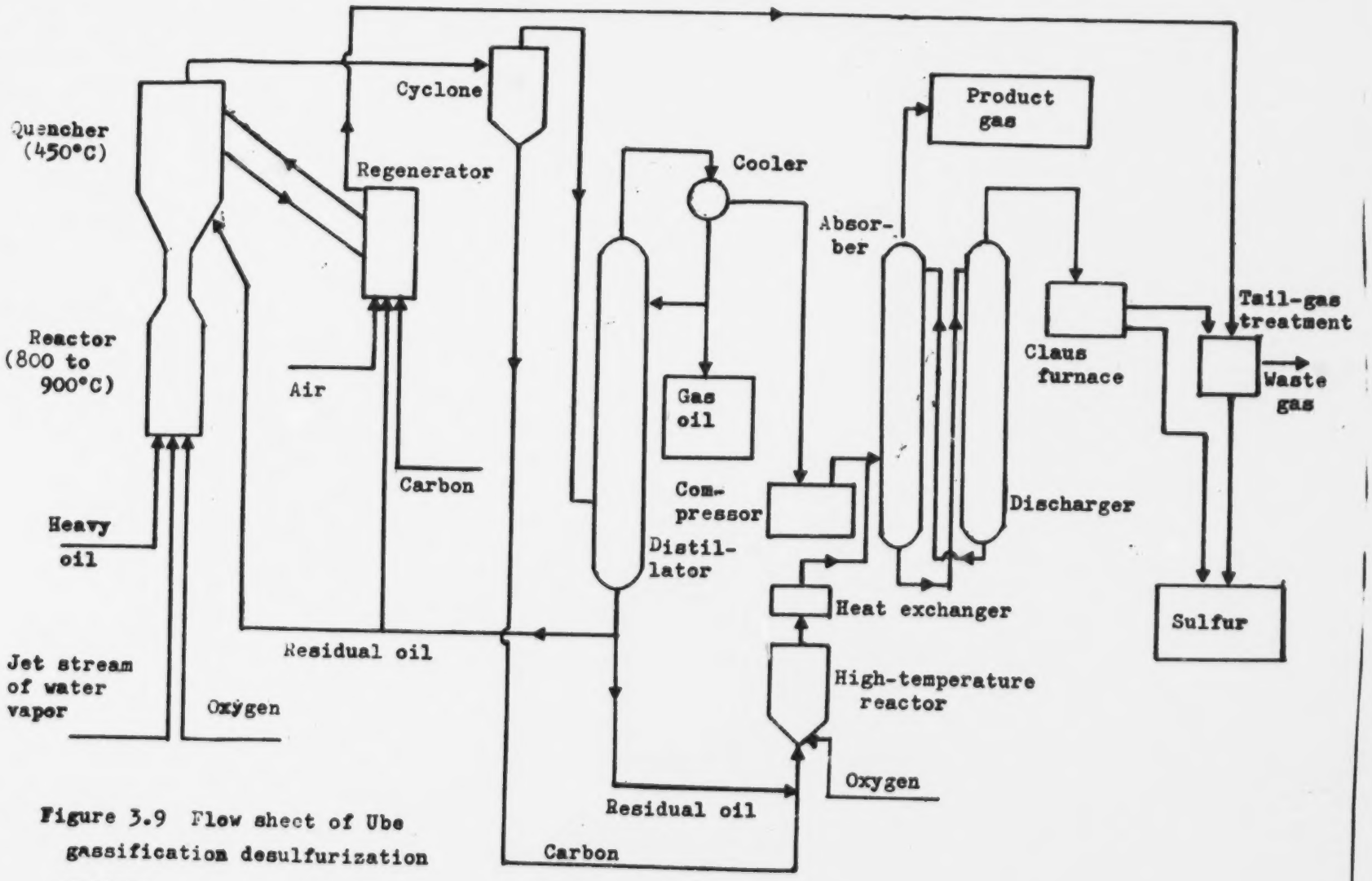


Figure 3.9 Flow sheet of Ube gassification desulfurization process

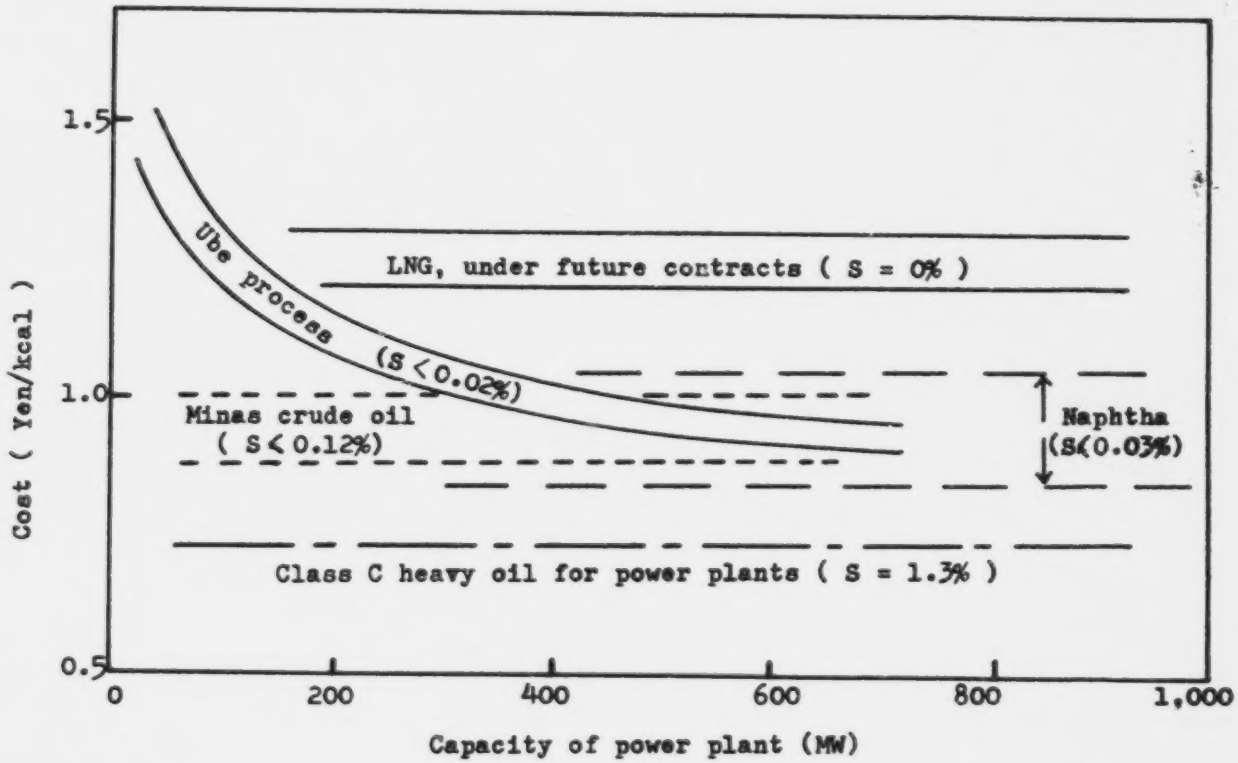


Figure 3.10 Cost and sulfur content of fuels for power plants

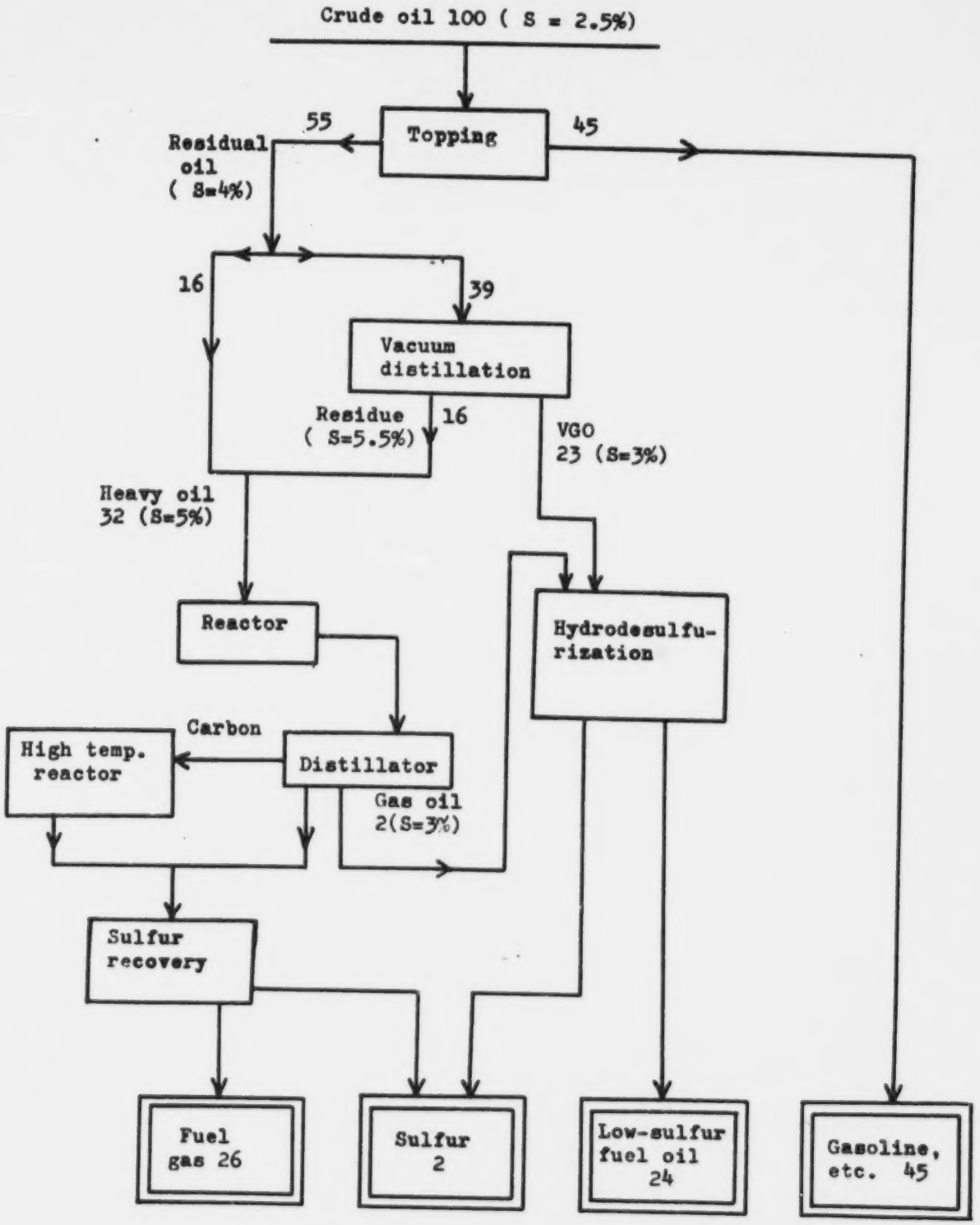


Figure 3.11 Combination of oil refinery and gasification desulfurization

3.7 Power generation by gasification desulfurization of heavy oil (Japan Gasoline process)[11]

Developer Japan Gasoline Co.(2-4, Otemachi, Chiyoda-ku, Tokyo)

State of development Feasibility study has been made recently by Japan Gasoline Co. A pilot plant may be built in 1972 jointly with Kansai Electric Power Co. or Tokyo Electric Power Co.

Description The process is similar to the Sulzer process of West Germany and consists of the following three steps:

(1) Partial oxidation and heat recovery--Heavy oil or asphalt is submitted to partial oxidation with air at 1,500°C under 10 to 30kg/cm^2 pressure to be converted into a gas mixture of hydrogen and water vapor (15%), carbon monoxide (22%), hydrogen sulfide (0.3%), nitrogen (60%) and other minor components. The gas is cooled to 160°C by generating high-pressure steam.

(2) Recovery of sulfur--More than 90% of the hydrogen sulfide is removed from the cooled gas and converted into elemental sulfur by a conventional process.

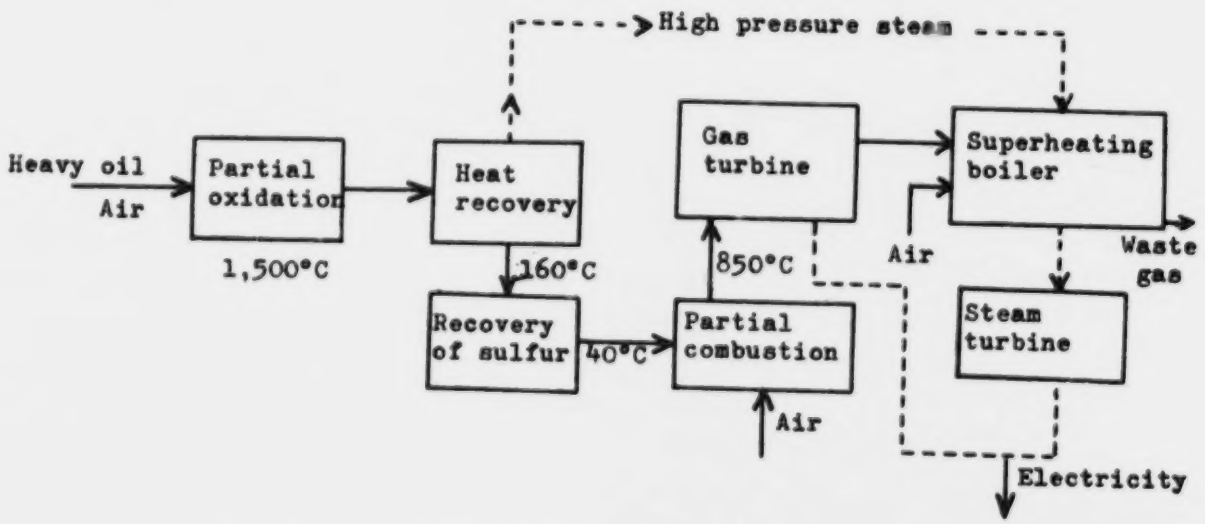


Figure 3.12 Simplified flow sheet of Japan Gasoline process

(3) Power generation--The desulfurized gas is partially burned by air to raise the temperature to 850°C, then sent to a gas turbine for power generation. The gas is then completely burned in a boilor to heat the high-pressure steam from the heat recovery section. The super-heated steam is used for a steam turbine to generate power. For partial oxidation, a Shell-type or Texaco-type reactor may be used. The total investment cost for a commercial-scale plant to generate 200MW electric power is estimated to be about ¥10 billion. The overall efficiency (power at terminal)/(LSV consumption) would be about 37.5%.

Advantages

Asphalt, a cheap fuel containing much sulfur, can be also used. A small amount of carbon formed by the partial oxidation can be completely recovered and recycled to obtain a clean fuel gas.

Sulfur in the fuel can be converted into hydrogen sulfide, which is readily removed.

More than 90% of sulfur can be removed.

The whole system is a combination of several well-established processes.

Emission of NO_x is less due to the low combustion temperature.

The amount of gas formed by the partial oxidation is about half that by complete combustion (Table 3.13). The actual volume of the gas for gasification desulfurization is only one-twentieth to one-sixtieth that for flue-gas desulfurization because the desulfurization is carried out under pressure. Plant size can be substantially reduced.

Table 3.13 Comparison of desulfurization processes (200MW plant)

	Gasification	Flue gas
Volume of gas (Nm^3/hr)	300,000	600,000
Sulfur compounds (% in gas)	H_2S 0.32	SO_2 0.15 to 0.17
Temperature (°C)	40	40 or higher
Pressure	10 to 30kg/cm^2	atmospheric

Disadvantages

Equipment that withstands high pressures is needed.

The generated gas, containing much nitrogen, has a low calorific value.

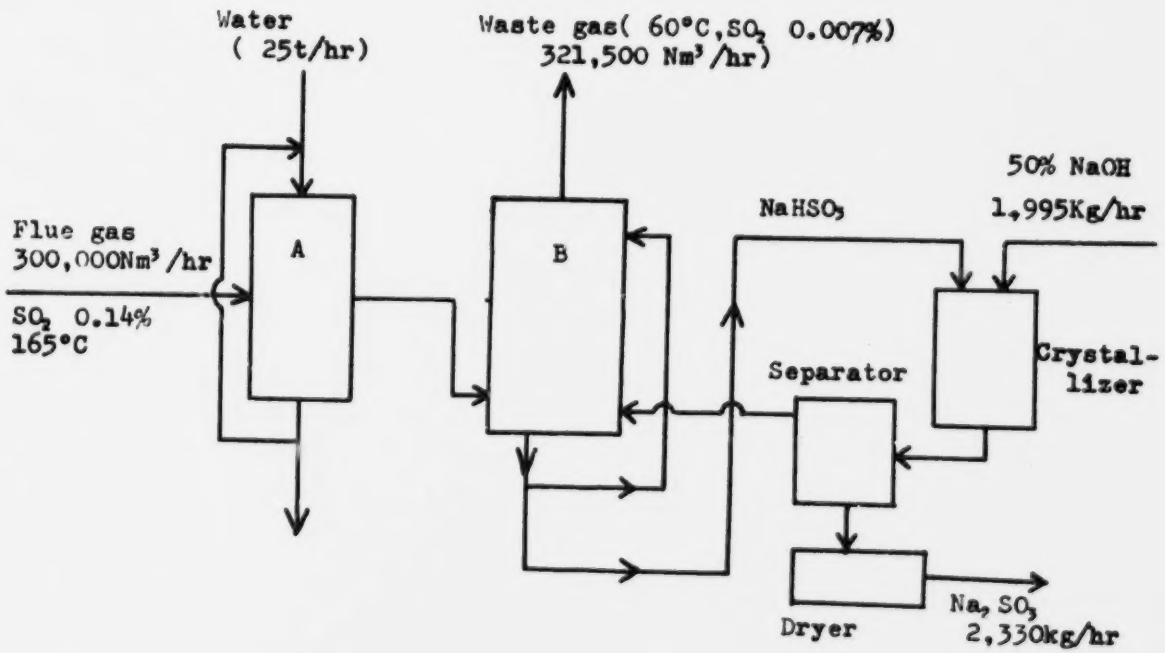
4 Stack-gas desulfurization by wet process

4.1 Kureha process (sodium scrubbing)[11, 12]

Developer Kureha Chemical Industry Co.
1-8, Horidomecho, Nihonbashi, Chuo-ku, Tokyo

State of development A commercial plant to desulfurize 200,000 to 300,000Nm^3/hr flue gas from an oil-fired power plant has been in operation since February 1969. Another plant of nearly equal size has been in operation since September 1970. Two more plants will be built in 1972.

Description Stack gas is first washed with water in a conventional scrubber for dust removal and cooling, then desulfurized with a sodium sulfite solution in a rubber-lined packed tower to remove about 95% of SO_2.



A : Dust removal and cooling B : Absorber

Figure 4.1 Flow sheet of Kureha process

The sodium bisulfite solution leaving the packed tower is treated with a sodium hydroxide solution to give a sodium sulfite solution, which is concentrated in a crystallizer to produce sodium sulfite crystals. The crystalline sodium sulfite is separated, dried, and supplied to paper mills. The purity of the sulfite ranges from 90 to 97%. The mother liquor (sodium sulfite solution) is sent to the packed tower.

The packed tower absorber was designed to evaporate as much water as the water in the sodium hydroxide solution charged, to maintain water-balance. Pressure drop in the absorber is 65mm H_2O. An oxidation inhibitor is used when it is necessary to reduce the sodium sulfate content of the product.

Table 4.1 Operation data

Amount of gas	Temperature in absorber		SO_2 concentration		Amount of liquid	
(Nm^3/hr)	Gas(°C)	Liquid(°C)	Inlet(%)	Outlet(%)	Charge (m^3/hr)	Discharge (m^3/hr)
233,000	61.5	62.0	0.135	0.007	31.5	30.6
218,000	59.5	59.5	0.134	0.009	32.0	31.0
227,000	60.0	60.0	0.125	0.010	31.1	29.6

Cost, advantages and disadvantages The total investment cost of the plant to treat 200,000 to 300,000Nm^3/hr gas was ¥420 million. The desulfurization cost including reheating of gas is ¥500 per kiloliter of heavy oil containing 2.8% sulfur (Table 6.7)

The process is simple and operation is easy.

The market for sodium sulfite, however, is limited. (6.1).

Modified process[11] Tests have been made to treat a sodium bisulfite solution with milk of lime or limestone to produce sodium sulfite and calcium sulfite. The sodium sulfite solution is recycled to the absorber. The calcium sulfite is oxidized into gypsum, which has a fairly large market in Japan.

$$2NaHSO_3 + CaCO_3 = Na_2SO_3 + CaSO_3 + H_2O + CO_2$$

$$CaSO_3 + 1/2\ O_2 + 2H_2O = CaSO_4 \cdot 2H_2O$$

Using this modified process, a demonstration plant capable of treating 5,000Nm^3 flue gas is under construction jointly with Kawasaki Heavy Industries at a cost of ¥50 million.

4.2 Showa Denko process (ammonia or sodium scrubbing)[11, 13]

Developer Showa Denko K. K.
34, Shiba Miyamotocho, Minato-ku, Tokyo

State of development Commercial plants designed to recover SO_2 from tail gas from sulfuric acid plants, and therefrom produce an ammonium sulfite solution for papermaking were operated for a few years. These plants were closed recently as the superannuated sulfuric acid plants were shut down.

A similar type commercial plant to treat 150,000Nm^3/hr flue gas from an oil-fired boiler using a sodium hydroxide solution in place of ammonia has been in operation since October 1970. Another plant of similar type to treat, with sodium hydroxide, tail gas (80,000Nm^3/hr) from a new sulfuric acid plant has been in operation since May 1971.

Description Vertical-cone type scrubbers are used. The liquid is charged from the bottom and blown up by gas to absorb SO_2. The liquid is recycled without the use of a pump. The liquid gas ratio is about 1 liter/m^3; gas pressure drop is less than 250mm H_2O. The desulfurized gas is discharged through a gas-liquid separator.

Two absorbers are used to treat 150,000Nm^3/hr of the gas from an oil-fired boiler, as is illustrated in Figure 4.3. The gas contains about 0.15% SO_2 and 0.12g/Nm^3 dust. About 95% of the SO_2 and 60% of the dust are removed.

The sodium sulfite solution is filtered to remove dust, after

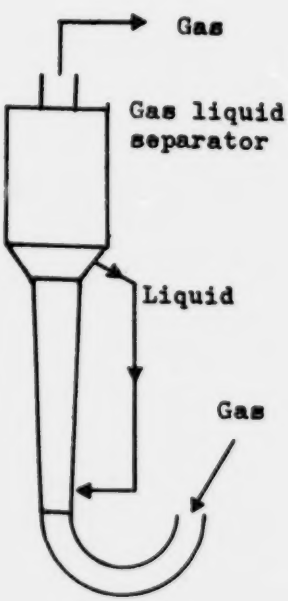


Figure 4.2 Type of scrubber

which it is sold to paper mills. The solution contains 20% sodium sulfite, less than 1% sodium sulfate, less than 0.05% sodium chloride, and less than 100g/m^3 heavy metals.

In the old plants which used ammonia, a small amount of white fume was generated which was not easy to remove by additional water scrubbing. This is the reason why sodium is used in the new plants which treat larger amounts of gas.

Economics The total investment for the plant to treat ~~150~~ 150,000 Nm^3/hr tail gas was ¥200 million. The operation cost is ¥680 per kiloliter of oil containing 2.7% sulfur.

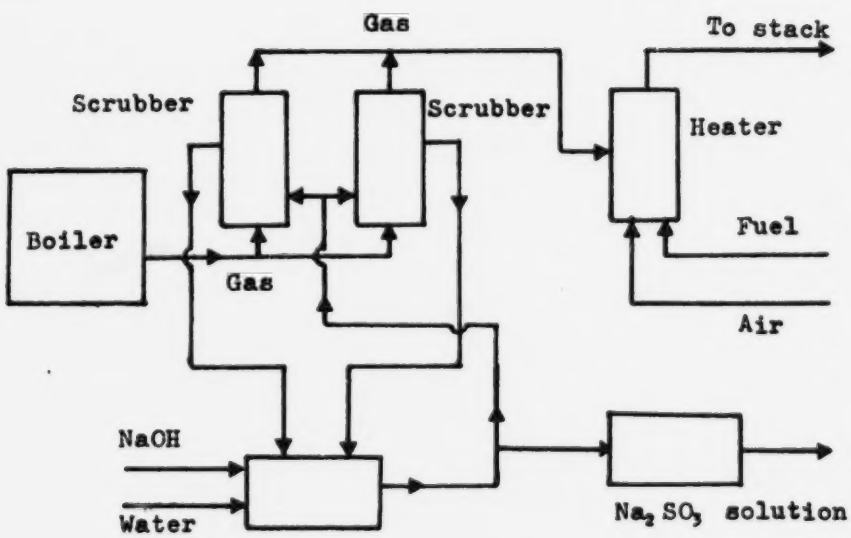


Figure 4.3 Flow sheet of Showa Denko process

4.3 Bahco-Tsukishima process (sodium scrubbing)[11, 12]

Developer Bahco (Sweden) and Tsukishima Kikai Co. (17-15, 2-chome, Tsukuda, Chuo-ku, Tokyo)

Description Desulfurization is carried out with a sodium hydroxide solution using the Bahco scrubber. About 95% of SO_2 is recovered as a sodium sulfite solution. More than 90% of dust is also removed. The solution is filtered to give a clear solution to be used for papermaking (Figure 4.4). Pilot plant tests have been made to produce solid sodium sulfite or sulfate. Tests also have been made to recover SO_2 with lime, to produce gypsum.

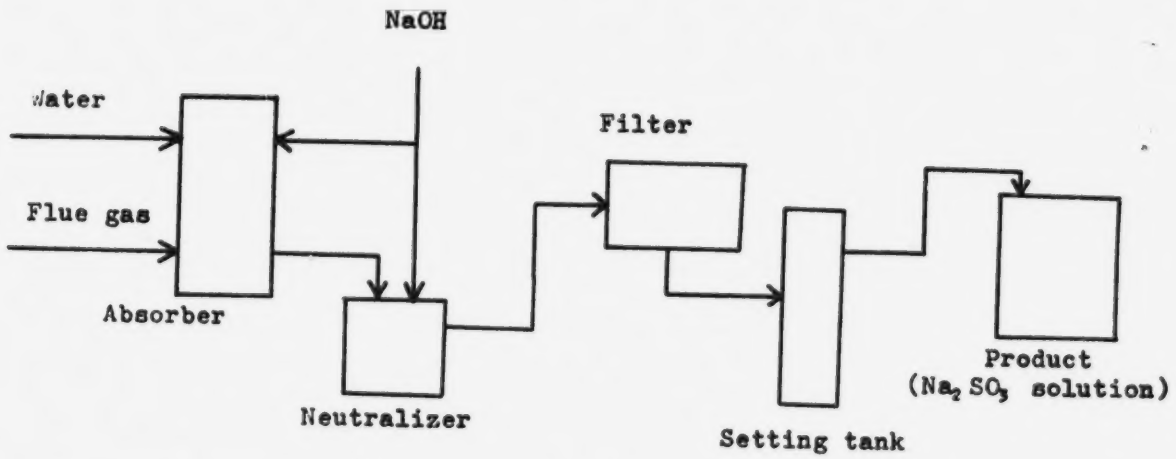


Figure 4.4 Flow sheet of Bahco-Tsukishima process

State of development Three commercial plants are in operation at Daishowa Paper Co. (Table 4.2).

Table 4.2 Commercial plants using Bahco-Tsukishima process

(Temperature of gas charged, 150 to 190°C
Temperature of gas discharged, 55 to 58°C
Pressure drop in scrubber, 360 to 380mm H_2O.)

	Plant site		
	Yoshinaga*	Suzukawa*	Suzukawa**
Flue gas (Nm^3/hr)	220,000	24,500	110,000
SO_2 in gas (ppm)	1,000	1,200	250 to 300
Dust (g/Nm^3)	0.01	0.01	0.15
SO_2 recovery (%)	95	95	90
Dust removal (%)	90	90	80
Number of scrubbers	3	1	1

* Oil-firing boiler ** Combustion gas of sludge

A plant is under construction at Central Glass Co. to treat 100,000Nm^3/hr combustion gas from its glass furnaces. Another plant is under construction at Daio Paper Co. to treat 300,000Nm^3/hr gas. In addition, several plants will be built to treat combustion gas of sludge from wastewater treatment in big cities such as Tokyo and Osaka. A lime scrubbing plant will be built at Yahagi Iron Co. Ltd.

4.4 Kanagawa PIL process (Jinkoshi process)[11, 12, 13]

Developer Industrial Research Institute of Kanagawa Prefecture
3173, Showamachi, Kanagawa-ku, Yokohama

Description A new type of absorber using screens has been developed by Kanagawa PIL (Jinkoshi). Sea water, industrial water, dilute aqueous ammonia, or sodium hydroxide solution flows down on the surface of stainless steel screens (about 10 mesh) placed vertically or with inclination to form stable thin liquid films which are highly effective for removal of SO_2 and dust.

Pilot plant tests A pilot plant with a capacity of 3,000Nm^3/hr of gas from an iron-ore sintering plant was built in 1967 at the Keihin works of Nippon Kokan (NKK). The gas was first treated by a conventional type of scrubber with water for cooling and then led into a scrubber with screens. More than 85% of SO_2 was removed by absorption with industrial

water at 33 to 35°C and pH 7.2 to 7.4. More than 95% of SO_2 was removed with very dilute aqueous ammonia (recovered from coke oven gas) at 36 to 41°C and pH 8.4 to 8.6 (Figure 4.5).

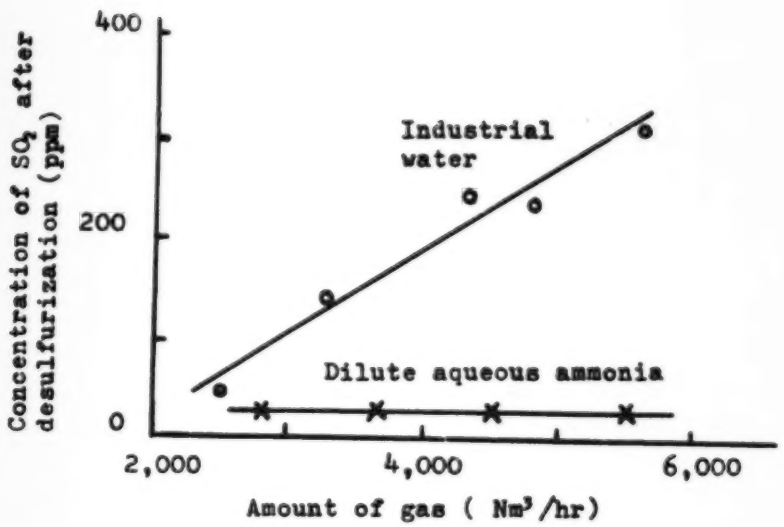


Figure 4.5 Desulfurization in pilot tests by Jinkoshi process
(SO_2 in gas 1,400 to 2,000ppm)

Larger pilot plant test A larger pilot plant designed to treat 30,000Nm^3/hr gas from an iron-ore sintering plant has been in operation since 1969 at the Keihin works of Nippon Kokan. The absorber, measuring 4.6 x 4.6 x 12.0m in size, consists of three sections: (1) a dust removal zone where most of dust is removed by sea water, (2) an SO_2 removal zone where SO_2 is absorbed by dilute aqueous ammonia (about 0.2% concentration) obtained from coke oven gas, and (3) an ammonia-gas recovering section where ammonia released in a small amount from the SO_2 removal zone is caught by sea water.

The water discharged from this section is sent to the dust removal section (Figure 4.6). The SO_2 concentration of the charged gas, 600 to 1,000ppm, was lowered to 50 to 80ppm when 30,000Nm^3/hr gas was treated with dilute aqueous ammonia at about pH 8. The investment cost for the plant was ¥80 million.

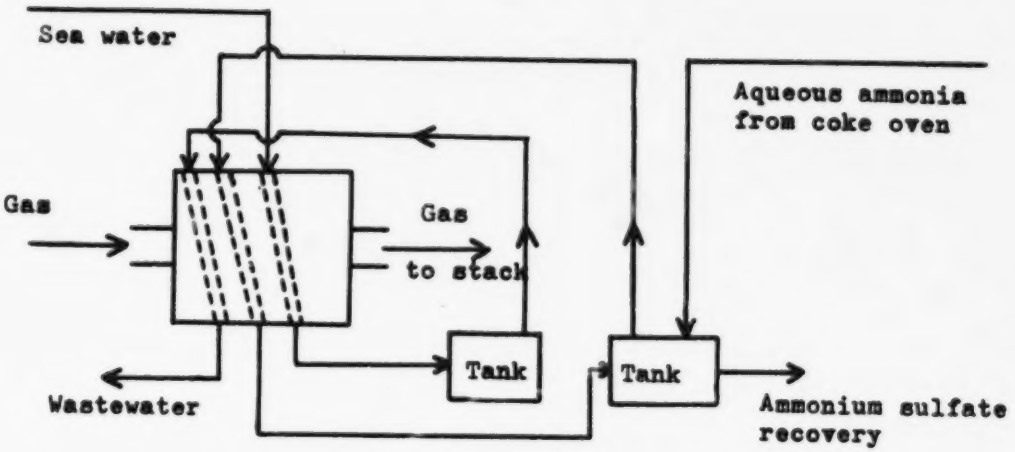


Figure 4.6 Flow sheet of pilot plant by Jinkoshi - NKK process (30,000 Nm^3/hr)

Prototype test (sodium scrubbing) A prototype plant to treat 45,000Nm^3/hr flue gas from an oil-fired boiler was built at Oji Paper's Tomakomai works in 1969 (Figure 4.7). The gas is first treated by a prescrubber in which screens (about 10 mesh) are placed nearly vertically to remove dust with water. The screens are set in frames about 1 meter wide and 2 to 3 meters long. The gas is then led into an absorber where screens are placed with inclination. A sodium hydroxide solution is fed onto the screen to absorb more than 90% SO_2 to form a solution of sodium sulfite and bisulfite.

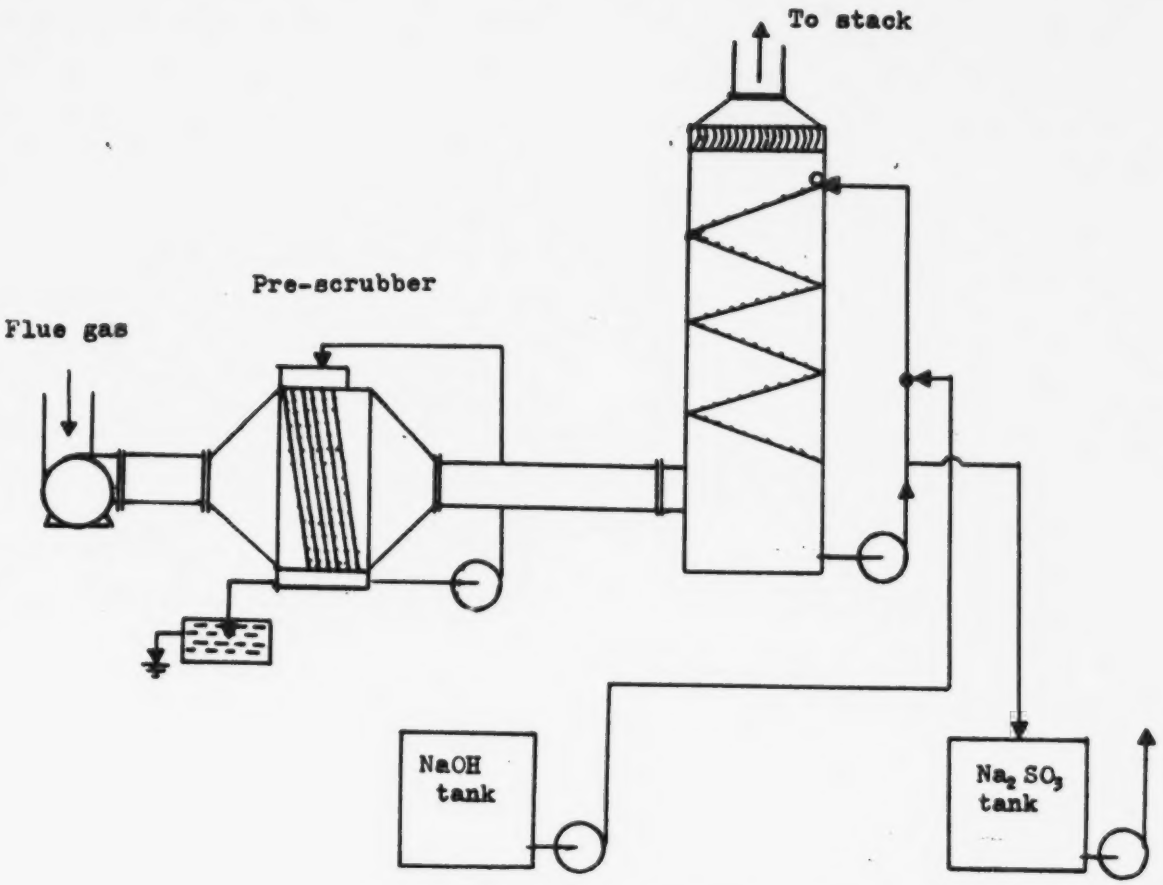


Figure 4.7 Prototype plant by Jinkoshi - Oji process ($45,000Nm^3/hr$)

Commercial plants The screen-type absorbers have been used commercially in the following plants:

(1) Tomakomai Plant, Oji Paper Co. (see 4.5).
(2) Kawasaki Plant, Nichimo Oil Co. Tail gas ($3,000Nm^3/hr$) from a Claus

furnace is treated with industrial water (60tons/hr). SO_2 concentration in the gas is reduced from 3,300ppm to 500ppm by an absorber with a pressure drop of 350mm H_2O. The wastewater containing SO_2 is mixed with other wastewater from the plant and discharged into the sea after pH adjustment.
(3) Tokuyama Plant, Tokuyama Soda Co. Waste gas (23,000Nm^3/hr) from a rotary kiln for cement production is desulfurized with sea water in order to utilize CO_2 in the gas for soda ash production.
(4) Keihin Works, Nippon Kokan (NKK). A plant designed to treat 150,000Nm^3/hr gas from an iron-ore sintering plant is under construction at an expense of ¥160 million as a joint venture of Nippon Kokan K. (NKK) and eight steel producers. An ammonium sulfite solution is used for the recovery of SO_2 to produce an ammonium bisulfite solution. The bisulfite solution is used to recover ammonia from coke oven gas (30,000Nm^3/hr) to produce an ammonium sulfite solution. A part of the sulfite solution is oxidized with air to produce ammonium sulfate; the rest is used to absorb SO_2.
(5) In addition, more than twenty smaller commercial plants are in operation or under construction at chemical, food and other manufacturers.

Advantages and disadvantages High recovery of SO_2 is attained with a slight pressure drop.

The degree of desulfurization can be varied easily by changing the number of the screens.

Uniform distribution of gas is required in order to ensure high recovery of SO_2 and low corrosion of screen.

4.5 Oji process (sodium scrubbing)[11, 13]

Developer Oji Paper Co.
4-7-5, Ginza, Chuo-ku, Tokyo

Description Wet-scrubbing of flue gas with a sodium hydroxide solution has been carried out by Oji Paper Co. commercially in several plants. A sodium sulfite solution is produced and is used for paper production. Two types of scrubbers, OK (cyclonic, over 85% recovery of SO_2) and Jinkoshi (screen type, over 90% recovery, see 4.4) are used.

Application The OK scrubber was originally designed for treatment of flue gas from a Kraft recovery boiler to recover sodium sulfate dust and SO_2. The Jinkoshi scrubber is designed to remove dust and SO_2 in gas from various plants.

State of development

OK scrubber Sixteen scrubbers of this type are in commercial use. A sodium sulfite solution is sprayed in a cyclonic scrubber to remove dust and SO_2. For example, a scrubber made of fiber-reinforced plastic, 4 meters in diameter and 15 meters high, can treat as much as 175,000Nm^3/hr of flue gas from a Kraft recovery boiler to absorb more than 85% SO_2 (Figure 4.8). Stainless-steel scrubbers are used for flue gas from oil-fired boilers.

Jinkoshi scrubber A pilot-scale scrubber has been in operation since 1970. A commercial-scale scrubber (220,000Nm^3/hr) has been completed very recently. Two more of the same capacity are under construction. In the pilot plant two Jinkoshi scrubbers are used in series; the first one for removal of dust and SO_3 mist. The first scrubber was omitted in the commercial plants. One scrubber removes more than 95% of SO_2 and most of dust. The dust is separated from the sodium sulfite solution.

Table 4.3 Commercial plants by Oji process

Type of scrubber	User	Plant site	Number of scrubbers	Gas		Date of completion
				Nm^3/hr	Temp. (°C)	
OK	Oji	Kasugai	8	1,068,000	150	1966 to 69
OK	Tokai		3	374,000	150	1970
OK	Oji	Kasugai	1	183,000*	170	1970
OK	Chuetsu	Sendai	1	116,000	150	1971
OK	Honshu	Kushiro	2	260,000	140	1971
OK	Oji	Ebetsu	1	184,000*	198	1971
Jinkoshi	Oji	Tomakomai	1	45,000*		1970
Jinkoshi	Oji	Tomakomai	3	660,000*		1971 to 73

* For oil-burning boilers. Others are for Kraft recovery boilers.

Advantages The OK scrubber is simple and cheap. It features a small pressure drop (40 to 60mm H_2O).

The Jinkoshi scrubber is quite effective for SO_2 recovery, with a very small pressure drop and power consumption.

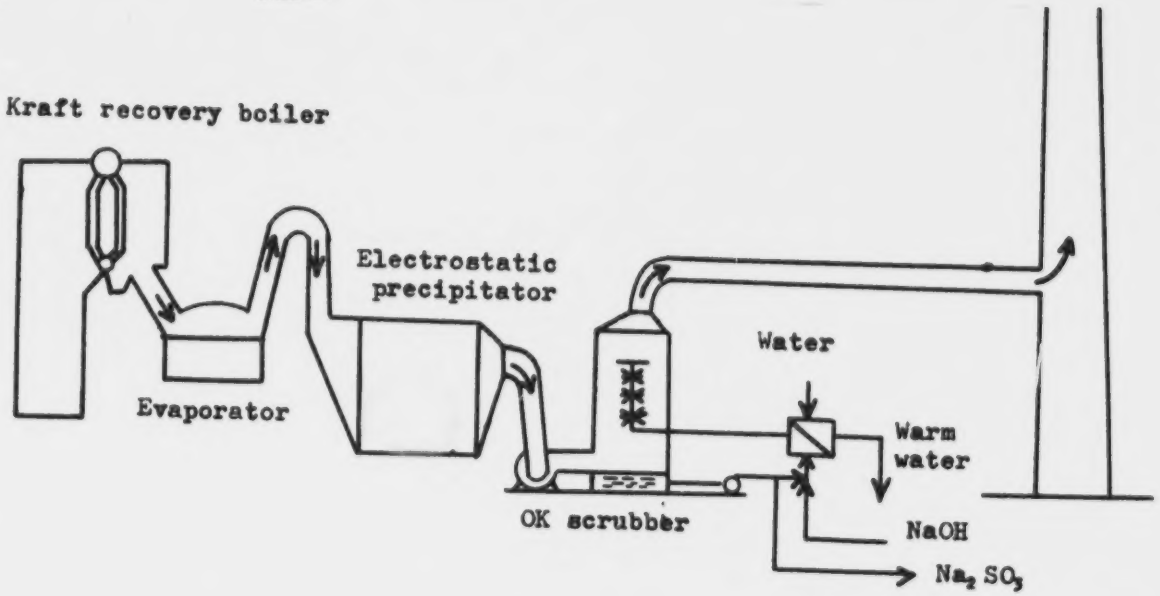


Figure 4.8 Flow sheet of Oji process

4.6 Wellman-Lord process (MKK)[14, 15]

Constructor Mitsubishi Chemical Machinery (MKK)
6-2, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Users Japan Synthetic Rubber, Chiba Plant

Description A commercial plant designed to treat 200,000Nm^3/hr flue gas from an oil-fired boiler has been in operation since June 1971. The flow sheet of the process is shown in Figure 4.7. Flue gas containing about 2,100ppm SO_2 is first washed in a scrubber--placed in a lower part of an absorber--to remove most of dust and SO_3. The gas is then washed with sodium sulfite solution to remove more than 90% of SO_2 and then led into a demister at the top of the absorber. The waste gas at 60°C containing about 200ppm SO_2 is reheated to 100 to 130°C by means of an after-burner.

Two absorbers are used in parallel. The sodium bisulfite solution formed in them is led into a double-effect evaporator-crystallizer and heated

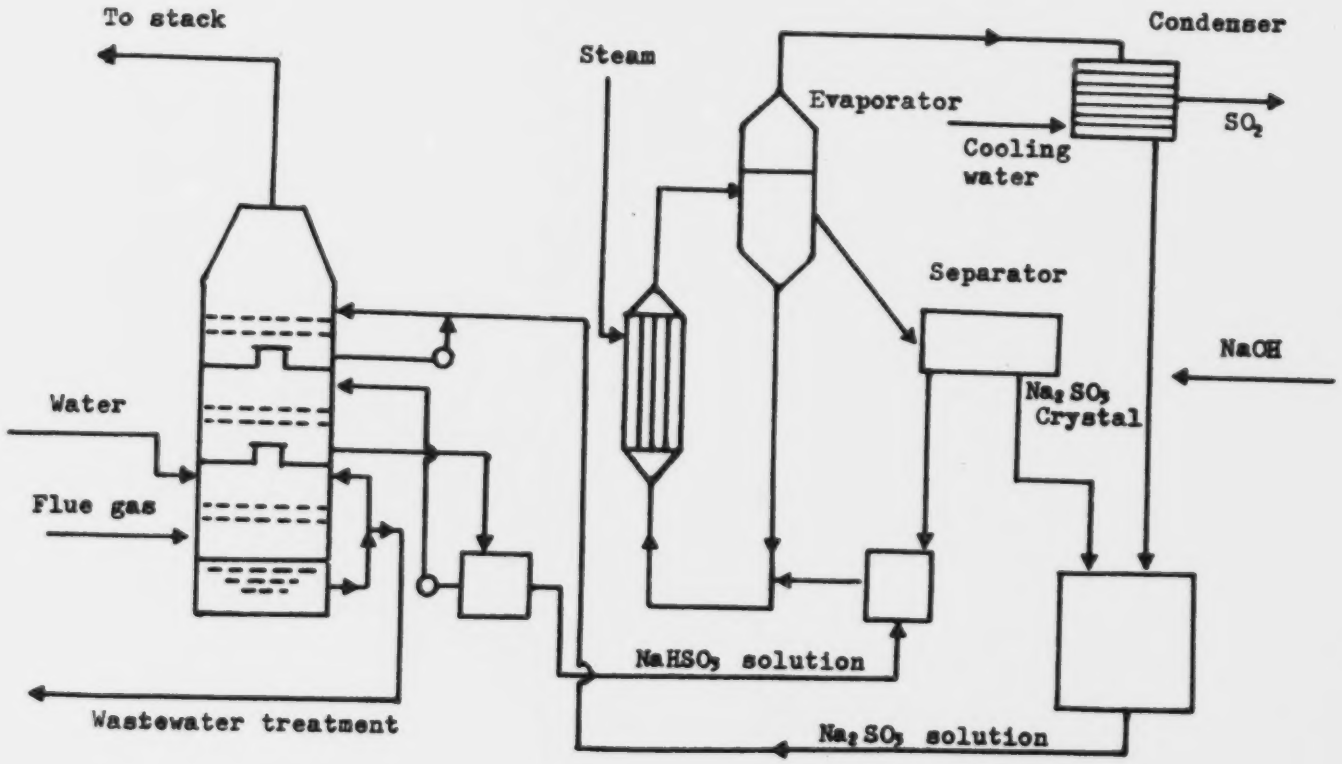


Figure 4.9 Flow sheet of Wellman - MKK process

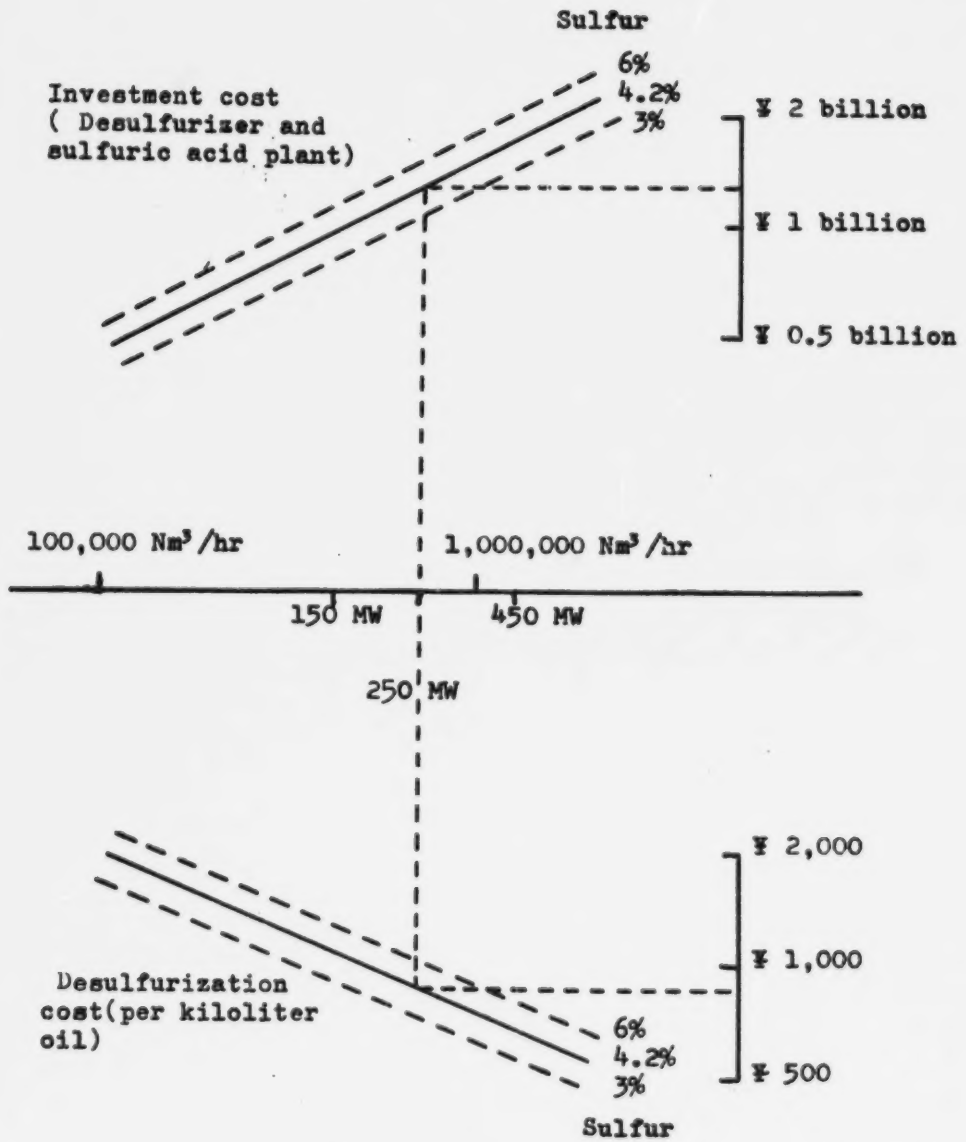


Figure 4.10 Relationship of plant size and sulfur content of oil to investment and desulfurization costs

to 100°C with steam, to be decomposed into a gas mixture of SO_2 and water vapor, and crystals of sodium sulfite.

$$2NaHSO_3 \rightleftharpoons Na_2SO_3 + SO_2 + H_2O$$

The gas mixture is cooled in a condenser to separate SO_2 from water. The product SO_2 is sent to a sulfuric acid plant to produce 40 tons sulfuric acid per day.

The sodium sulfite crystals are centrifuged from the mother liquor, dissolved into the condensate from the condenser, and recycled to the absorbers. The mother liquor is returned to the crystallizer. Sodium sulfate formed by oxidation is removed from the liquor.

Economics The total investment cost including the cost for the sulfuric acid plant was ¥800 million. The relationship of plant size and sulfur content of oil to investment and operation costs are illustrated in Figure 4.10 (see also Tables 6.7 and 6.8).

4.7 Wellman-Lord process (SCE)[11]

Constructor Sumitomo Chemical Engineering
33-5, 3-chome, Hongo, Bunkyo-ku, Tokyo

User Toa Nenryo, Negishi Plant

Description A commercial plant designed to treat tail gas (70,000Nm^3/hr) from a Claus furnace has been in operation since July 1971. The flow sheet of the process is shown in Figure 4.11.

The tail gas at 500°C containing about 7,000ppm SO_2 is cooled to 350°C in a waste-heat boiler, then cooled to 100°C in a cooling tower with water spray. This cooling method was used because gas containing much SO_2 at 100 to 350°C is quite corrosive. The gas at 100°C is then cooled to 70°C in a heat exchanger and introduced into an absorber with a three-stage sieve tray to which a sodium sulfite solution at pH 6.2 to 6.4 is charged. About 93% of SO_2 is recovered in the absorber.

Sodium bisulfite solution at pH 5.7 to 6.0 is discharged from the absorber, led to an evaporating crystallizer, and heated to 100°C to separate a gas (50% SO_2 and 50% water vapor) and crystalline sodium sulfite from the solution. The gas is cooled in a condenser to remove water. The product gas which contains more than 99% SO_2 is sent to a Claus furnace. The solid sodium sulfite is dissolved in water from the condenser and

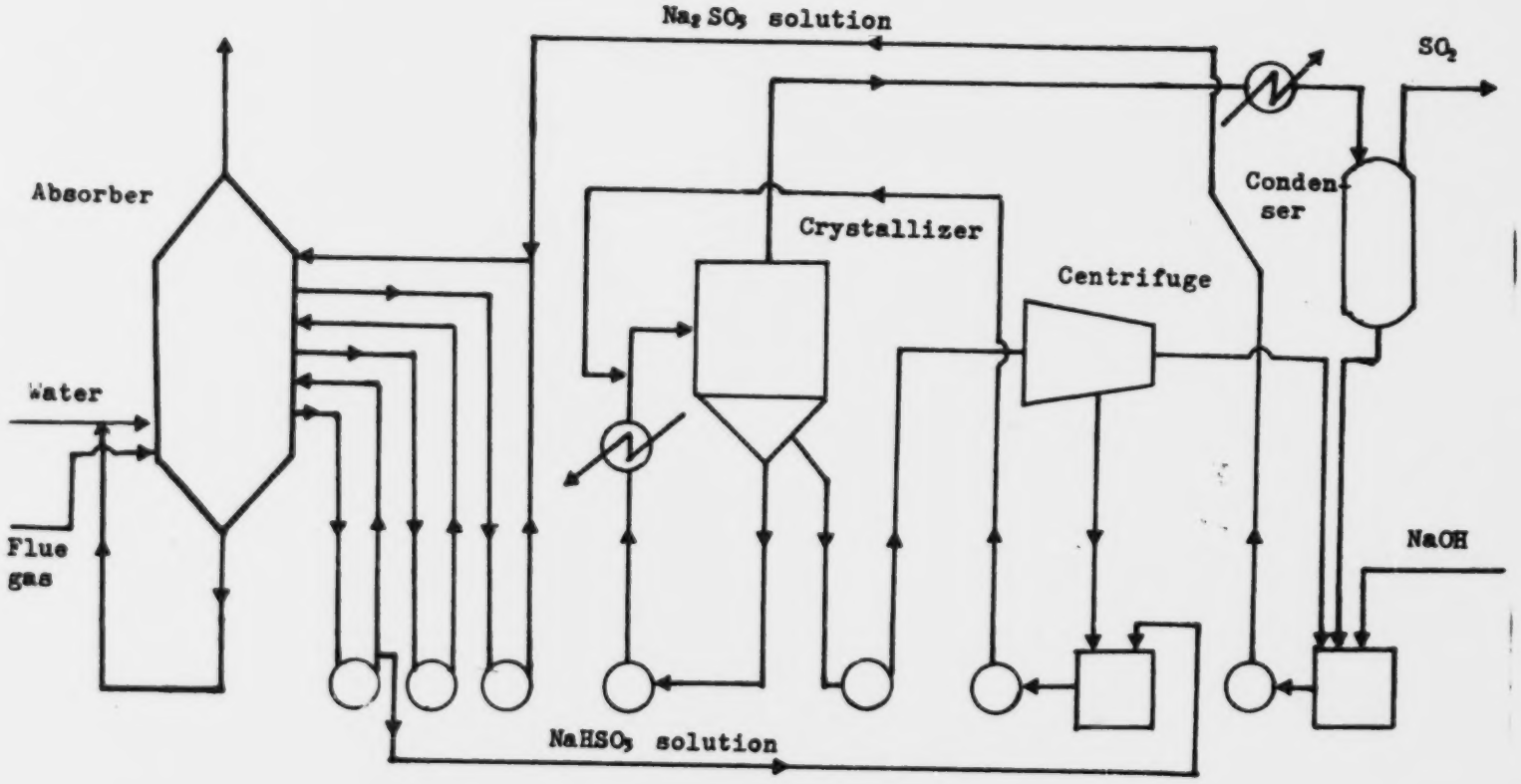


Figure 4.11 Flow sheet of Wellman - SCE process

returned to the absorber. The remaining solution is recycled to the crystallizer. A portion of the solution is taken out of the system to remove impurity and the sodium sulfate formed by oxidation.

An oxidation inhibitor developed by Sumitomo Chemical Co. has been used in the process. Without the inhibitor 3 to 5% of total sodium compounds in the plant is converted into sulfate in a day. By the use of the inhibitor, oxidation is reduced to about one-third resulting in a substantial decrease in the consumption of sodium hydroxide.

The waste gas from the absorber is emitted at 60°C without reheating. Although there has been no problem involving the waste gas, it is planned to heat the gas by some means for safety.

Acid-resisting materials such as stainless steel, fiber-reinforced plastics and plastic coatings are used in the plant. Tests have been made to seek cheaper acid-resisting materials. Tests also have been made to recover sodium hydroxide from by-product sodium sulfate.

Economics The total investment cost for the recovery plant was ¥600 million. In addition, ¥200 million was required for the cooling system for the tail gas including a waste-heat boiler, cooling tower, and heat exchanger.

It is estimated by Sumitomo Chemical Engineering that when this type of desulfurization plant is used for a 250MW oil-fired power plant to treat 750,000Nm^3/hr flue gas, the operation cost to remove 90% of SO_2 would be about ¥1,500 per kiloliter of oil. Reheating of the waste gas by an after-burner would require ¥200 to 300 more.

4.8 Mitsubishi-JEC process (lime-gypsum process)[11, 12, 13]

Developer Mitsubishi Heavy Industries (5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo) and Japan Engineering Consulting Co. (1-4, Ogawamachi, Kanda, Chiyoda-ku, Tokyo)

Description The gas is first washed with water in a spray tower for dust removal and cooling to 50 to 60°C, then treated with milk of lime. In a commercial plant completed in 1967, a large spray tower was used for desulfurization to minimize the scaling problem. Extensive tests have been made by Mitsubishi to prevent scaling and to improve the scrubber, resulting in the establishment of many items of know-how for scale prevention. In new commercial plants which are under construction, plastic-grid packed towers are used. Two packed towers are used in series (Figure 4.12). Milk of lime is charged to the No. 2 absorber. The reaction

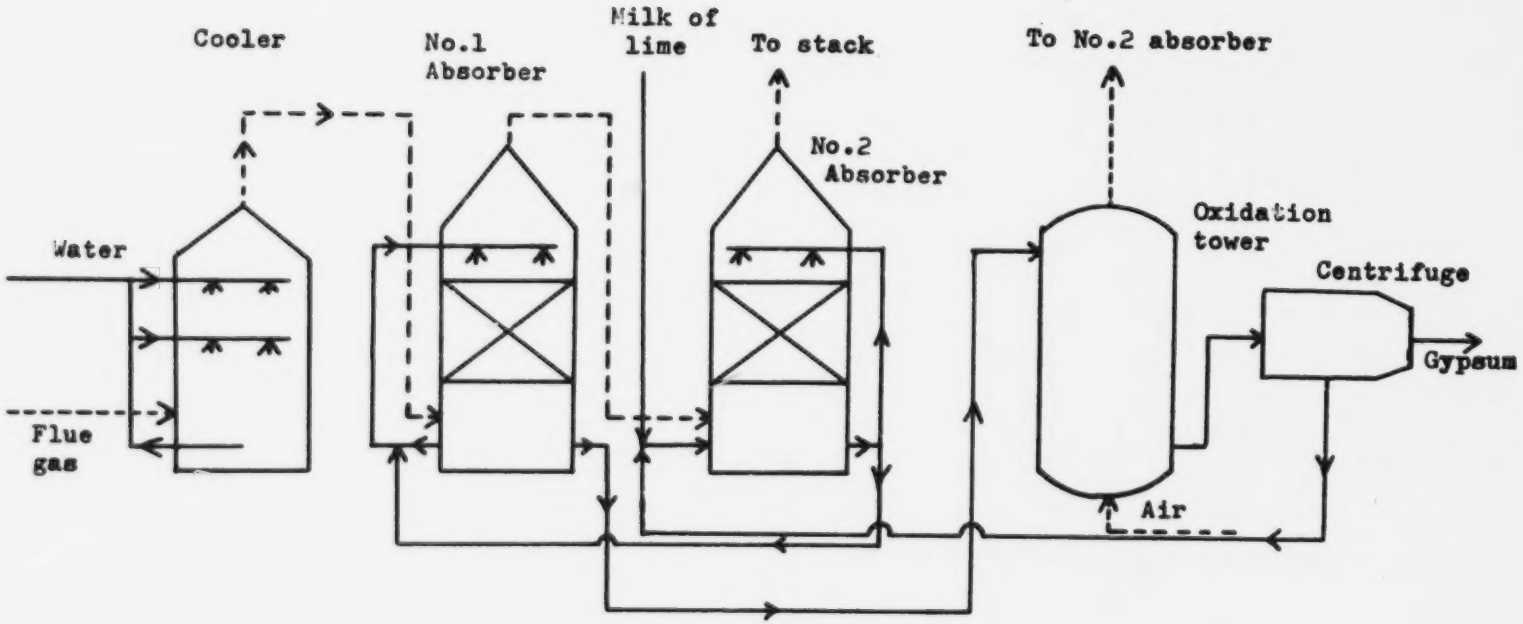


Figure 4.12 Mitsubishi-JEC lime-gypsum process

product, a mixture of calcium sulfite and lime with a small amount of gypsum, is led to the No. 1 absorber. Gas is first introduced into the No. 1 absorber and then to No. 2 absorber to attain more than 90% desulfurization. Calcium sulfite slurry at pH 4.0 to 4.5 is discharged from the No. 1 absorber and sent to an oxidation tower. In the tower the sulfite is converted into gypsum by oxidation with fine bubbles of air at 50 to 80°C under 5kg/cm^2 pressure. Very fine bubbles are produced by means of a rotary atomizer invented by Japan Engineering Consulting Co. Gypsum is centrifuged from liquor, the liquor is recycled to the No. 2 absorber. Gypsum thus obtained has more than 98% purity and good quality, which make it suitable for use in cement and gypsum board.

State of development

(1) A commercial plant (Koyasu plant, Nippon Kokan K.) to treat tail gas from a sulfuric acid plant 60,000Nm^3/hr containing 0.2 to 0.3% SO_2 has been in operation since 1967. A spray tower absorber (5m x 7m rectangular prism 15.5m high) is used to remove about 90% SO_2. Most of the units are provided with PVC lining. Pumps are made of hard rubber.

(2) A commercial plant to treat flue gas from an oil-fired boiler at the rate of 100,000Nm^3/hr is being built by Mitsubishi at the Amagasaki plant, Kansai Electric Power. A spray tower is used for cooling and dust removal; two grid packed towers are used for desulfurization. The plant, designed to reduce SO_2 concentration in the gas from 1,500ppm to 100ppm, is scheduled to come on-stream in March 1972.

(3) Another commercial plant to treat 52,000Nm^3/hr gas from a sintering plant of Tomakomai Chemical, Tomakomai, containing 1,800ppm SO_2 is under construction by Japan Engineering Consulting Co. The types of absorbers are the same as in (2) above. The plant is designed to reduce SO_2 to 50ppm (97% recovery). Liquid gas ratio of about 10 liter/Nm^3 will be used to attain the high recovery rate.

(4) Two other commercial plants are being planned.

Advantages The process is fairly simple. Good quality gypsum is obtained which can be sold for ¥2,000/ton. Rotary atomizer is quite effective for oxidation, involving no operational problem.

Disadvantages Oversupply of gypsum might occur within several years if too many gypsum-producing desulfurization plants are built.

Economics Investment cost for the Amagasaki plant to treat 100,000Nm^3/hr gas is ¥450 million. That for the Tomakomai Plant to treat 52,000Nm^3/hr gas is ¥100 million. The latter is unusually cheap.

Materials and utilities needed for a 250MW power plant (750,000Nm^3/hr gas) are shown in Table 4.4

Table 4.4 Materials and utilities for desulfurization of flue gas from 250MW power plant

(Sulfur in oil 3%, 90% recovery of SO_2)

Slaked lime	80t/day
Industrial water	1,000t/day
Sea water	3,000t/day
Electricity	70,000kWh/day
Sulfuric acid	3t/day
Labor	2 persons/shift
By-product gypsum	180t/day

The operation cost for a plant to treat 150,000 to 200,000Nm^3/hr gas from an oil-fired boiler is estimated by Mitsubishi at ¥1,400 to 1,800 per kiloliter of oil containing 2.5 to 3% sulfur, including revenue by selling the gypsum at ¥2,000/ton.

4.9 Chiyoda Thoroughbred 101 process[11)]

Developer Chiyoda Chemical Engineering & Construction
1580 Tsurumi-cho, Tsurumi-ku, Yokohama

Outline of the process Flue gas is washed with dilute sulfuric acid which contains a catalyst and is saturated with oxygen. SO_2 is absorbed and converted into sulfuric acid. Part of the acid is reacted with limestone to produce gypsum. The rest is diluted with gypsum wash water and returned to the absorber.

Description The flow sheet is shown in Figure 4.13. Flue gas is first treated by a wet scrubber to eliminate dust and to cool the gas to 60°C. The cooled gas is led into a packed tower absorber containing 1 inch Telleretts. Dilute sulfuric acid (2 to 10% H_2SO_4) which contains a soluble catalyst and is nearly saturated with oxygen is fed to the packed tower. About 90% of SO_2 is absorbed, and partly oxidized into sulfuric acid.

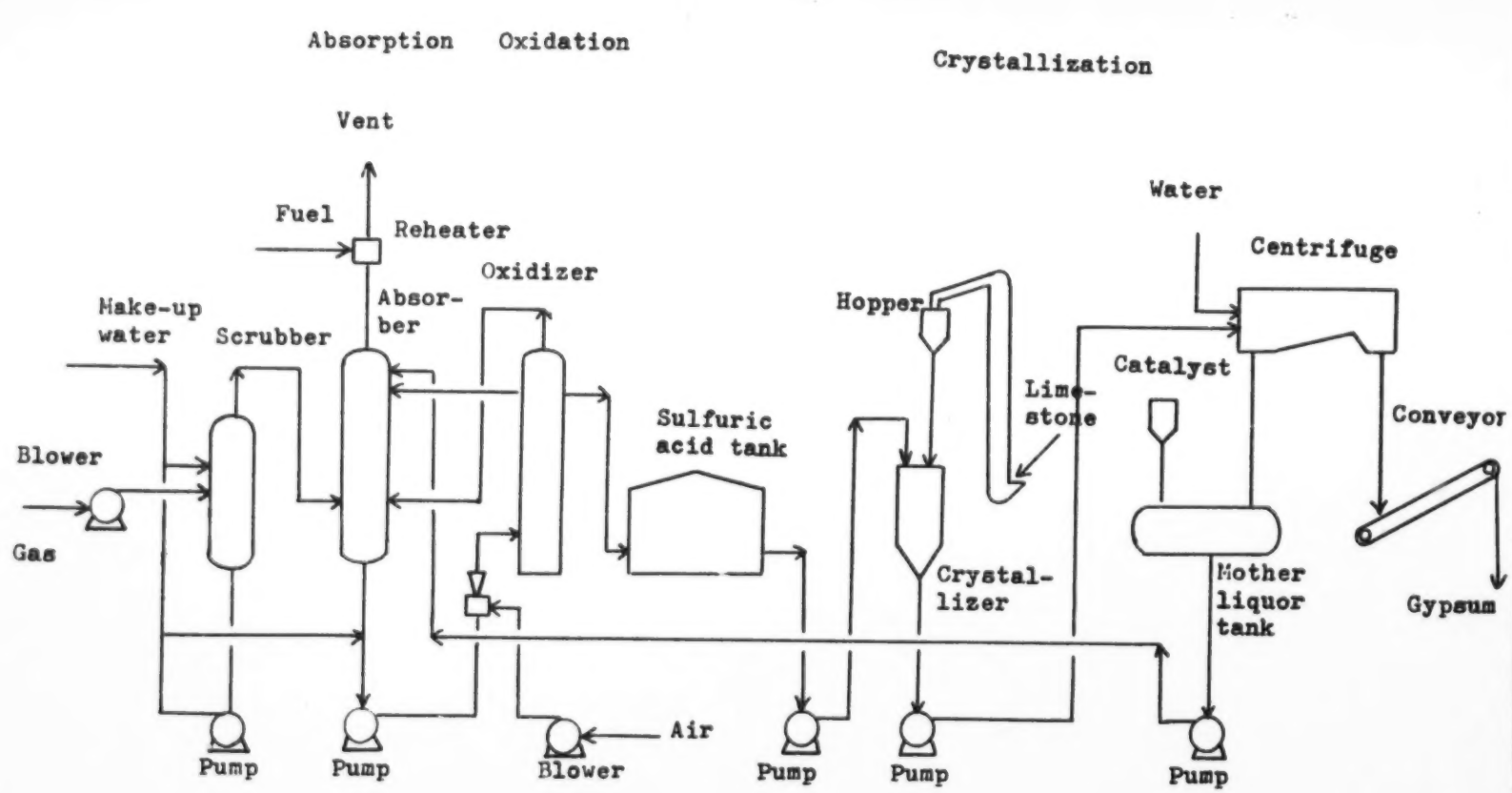


Figure 4.13 Chiyoda Thoroughbred 101 process

The product acid is led to the oxidizing tower into which air is bubbled from the bottom for oxidation. Most of the acid nearly saturated with oxygen is returned to the absorber. Part of the acid is treated with powdered limestone (minus 200 mesh) at 50 to 55°C to produce gypsum. A special type of crystallizer has been developed to obtain good crystals of gypsum 100 to 300 microns in size. The gypsum is centrifuged from the mother liquor and washed with water. The product gypsum has good quality and is salable.

The mother liquor and wash water are sent to the absorber. The amount of the wash water is equal to the amount of water evaporated and lost from the absorber.

Operation data of pilot plant Chiyoda has operated a pilot plant with a 1,000Nm^3/hr capacity for several months continuously without trouble. The absorber is 700mm in diameter and 6 meters high. Oil-burning gas with 1,300ppm SO_2 and 1.0mg/Nm^3 dust is treated to decrease the SO_2 content to 100ppm and the dust content to 0.01g/Nm^3. The waste gas temperature is about 55°C. The gas is heated and released through a stack. The by-product gypsum contains about 97% dihydrate and about 0.6% limestone with no sulfite.

A fiber-reinforced plastic is used for the towers and pipings. Loss of catalyst is virtually zero. The catalyst is kept a secret, but is said to be an inexpensive material.

State of development A commercial plant will be built in Mizushima, Nippon Mining Co. by September 1972 to treat tail gas (0.8% SO_2) from a Claus furnace at the rate of 35,000Nm^3/hr. In the plant 50 tons of gypsum will be produced daily. Another plan is afoot to build a plant to treat 400,000Nm^3/hr flue gas from oil-burning boilers. In the commercial plant the towers will be provided with rubber or FRP linings.

Advantages The process is simple and the plant is easy to operate. Even in the event that the gypsum-producing system has to be stopped for a day or two for repairs, the absorbing system can be operated continuously. The concentration of sulfuric acid increases by 1 or 2% in this case but SO_2 recovery is not decreased. Catalyst is cheap and is not poisoned by impurities in the gas.

Disadvantages A fairly large absorber is required as shown in the following table. Large pumps are also required.

Table 4.5 Size of towers (meters)

Amount of gas(Nm^3/hr)	Absorber		Oxidizer	
	Diameter	Height	Diameter	Height
200,000	9	15	4.6	19
500,000	15	15	6.4	19

Table 4.6 Investment and desulfurization costs
(SO_2 content of gas 1,500ppm, 90% recovery)

	Amount of gas (Nm^3/hr)	
	200,000	500,000
Investment cost (millions of yen)	540	980
Annual cost (millions of yen)		
Fixed cost[1]	9.9	18.6
Operation cost[2]	9.8	19.9
Revenue from gypsum sale[3]	3.5	8.9
Desulfurization cost (yen/ton of oil)	1,200	880

1) Including depreciation (14.3% of investment) and interest.

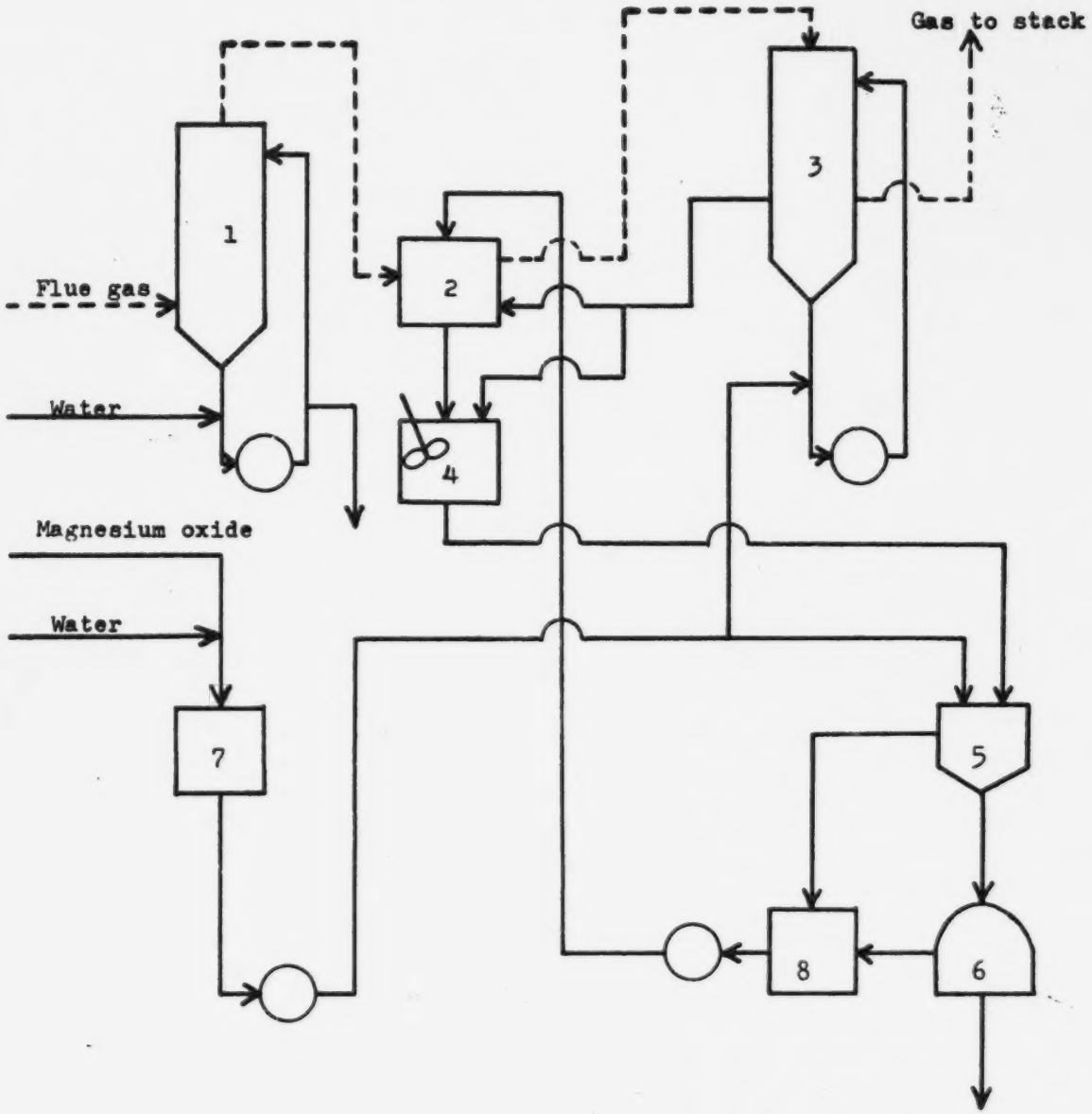
2) Limestone ¥2,000/ton. Electricity ¥3/kWh. Water ¥5/ton. Costs for catalyst, labor, repairs, and managing included.

3) Sale price of gypsum ¥2,000/ton.

4.10 Kawasaki magnesium process[11, 13]

Developer Kawasaki Heavy Industries Ltd.
16-1, 2-chome, Nakamachidori, Ikeda-ku, Kobe

Description The process resembles the Chemico process. Magnesium hydroxide from sea water is used for absorption of SO_2. Two absorbers arranged in series give large crystals of magnesium sulfite (Figure 4.14). The sulfite formed in the second absorber is further reacted with SO_2 in the first absorber to form magnesium bisulfite. The sulfite is then



1 : Cooler 2 : First absorber 3 : Second absorber
4 : Crystallizer 5 : Precipitator 6 : Centrifuge
7 : Magnesium hydroxide tank 8 : Mother liquor tank

Figure 4.14 Flow sheet of Kawasaki magnesium process

treated with magnesium hydroxide in a crystallizer and a precipitator to produce large crystals (300 to 500 microns) of sulfite which is readily separated from the mother liquor and also from small crystals of magnesium hydroxide. The sulfite separated is calcined to regenerate the magnesium oxide and to release SO_2. The oxide is recycled to the absorber; SO_2 is used for sulfuric acid production.

State of development This process was invented by Mr. S. Akimoto, Osaka Kobai K. K. (Japanese Patent 577,195 July 6, 1970. Patent application was made in July 1966). Kawasaki bought the patent and, since September 1971, has operated a pilot plant of the absorbing step which is capable of treating 5,000Nm3/hr flue gas. Pilot plant tests for the regeneration step will start in January 1972.

4.11 Grillo process[11, 12, 13)]

Developer Grillo Werke, West Germany
Mitsui Shipbuilding Co.
5-6-4, Tsukiji, Chuo-ku, Tokyo

State of development Mitsui has bought the SO_2 absorption process from Grillo and now operates a pilot plant to treat 1,200Nm3/hr gas from oil-fired boilers.

Description The process consists of an absorption step and regeneration step. Flue gas is desulfurized by a spray of slurry containing magnesium and manganese oxides to form sulfides and sulfates of both magnesium and manganese. The reaction product is dried in a spray dryer. The dried solid is charged into a furnace for heating at 950°C to release SO_2 and to regenerate magnesium and manganese oxides. The released SO_2 is used for sulfuric acid production. The presence of manganese promotes the decomposition of magnesium sulfate.

Mitsui has developed a special oil-fired furnace for the regeneration. The details are not published yet.

Cost estimation[12)] The investment cost for a commercial plant to treat 1,200,000Nm3/hr flue gas from a boiler burning heavy oil (5.5% sulfur) is estimated at ¥3.3 billion including the cost for a sulfuric acid plant. The desulfurization cost to remove 92% of SO_2 is estimated at ¥970/kiloliter oil, including depreciation over a 7-year period.

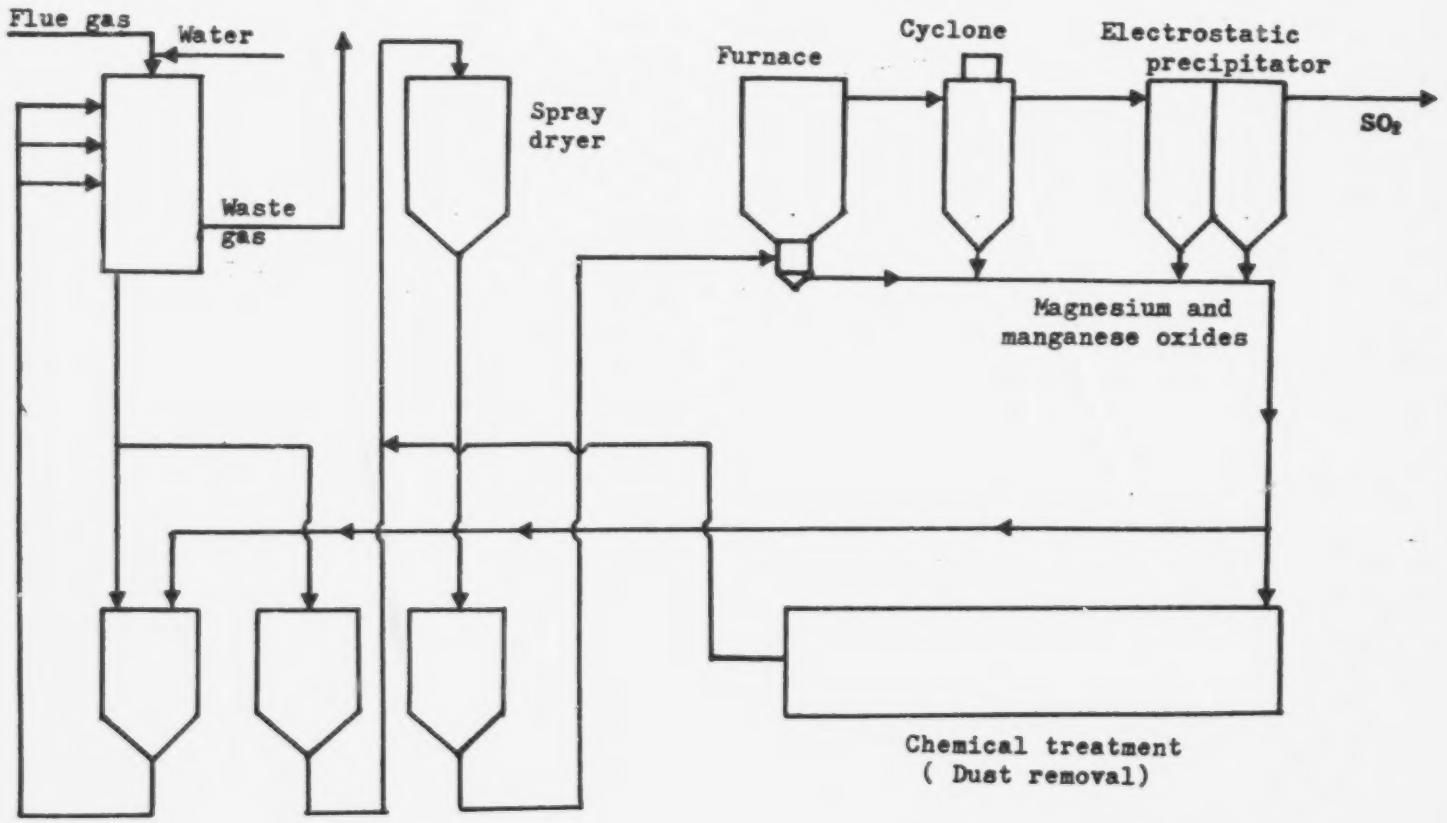


Figure 4.15 Grillo-Mitsui process

4.12 Chemico process (lime scrubbing and magnesium scrubbing)[11)]

Constructor Mitsui Miike Machinery Co.
2-1-1, Muromachi, Nihonbashi, Chiyoda-ku, Tokyo

Lime process A desulfurization plant designed to treat 512,000Nm^3/hr flue gas from a coal-fired boiler (165MW) is under construction at Omuta Works, Mitsui Aluminum Co. Operation will start in March 1972. The coal contains 2.5 to 3% sulfur. The power plant, equipped with an electrostatic precipitator, has been in operation for some time.

Chemico scrubbers (two-stage venturi) are adopted. A calcium hydroxide sludge from a plant producing acetylene from calcium carbide will be used as the absorbent for SO_2. The by-produced calcium sulfite will tentatively be used for land filling at the sea shore. Should any water-pollution problem occur, Mitsui Aluminum plans to install a facility for oxidation. This desulfurization plant will be the first large-scale one in Japan that does not produce salable by-products.

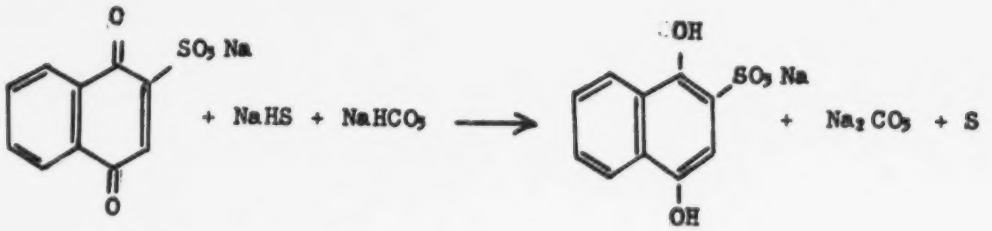
Magnesium process Mitsui Miike Machinery Co. has been operating a pilot plant designed to treat 2,500Nm^3/hr flue gas with magnesium hydroxide slurry. The details have not been published yet.

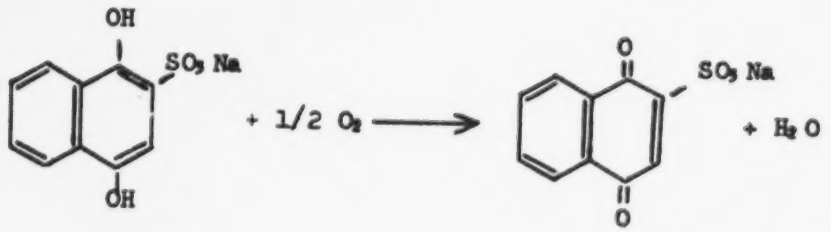
4.13 Takahax process (H_2S recovery)[11, 16)]

Developer Kinon Chemicals
3-3, 1-chome, Ginza, Chuo-ku, Tokyo

Description Hydrogen sulfide is recovered by an alkaline solution at pH 8 to 8.5 containing a newly developed catalyst 1,4-naphthoquinone-2-sulfonic acid, which precipitates elemental sulfur rapidly. The catalyst is readily regenerated by introducing air into the solution.

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3$$





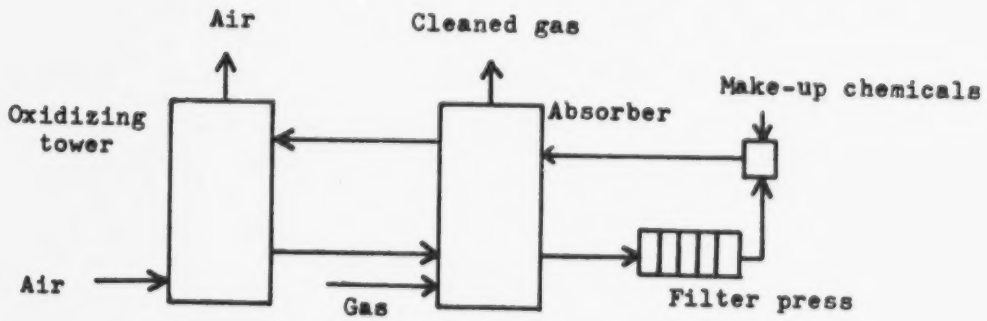


Figure 4.16 Two-tower system, Takahax process

More than 99.0% of hydrogen sulfide in coke oven gas, petroleum gas, etc. is recovered. 1,4-naphthoquinone is recovered easily from the sludge by-produced when phthalic anhydride is produced from naphthalene. It can also be directly synthesized at a high yield. It can be easily converted to 1,4-naphthoquinone-2-sulfonic acid, which is soluble in water. Two towers--absorber and oxidizing tower--are used for the cleaning of fuel gas, etc. For the desulfurization of waste gas, one tower is used into which both air and the gas containing hydrogen sulfide are introduced.

Operation data[11] The following values have been adopted recently as operating conditions.

Alkali concentration	40kg/kl as Na_2CO_3
pH	8 to 8.5
Catalyst concentration	1.5 to 2 moles/kl
Liquid-gas ratio	22 gas/liquid
Liquid-air ratio	0.55 liquid/air
Make-up chemicals	Catalyst: 0.02 mole/kg of recovered sulfur
	Alkali: 0.15kg/kg of recovered sulfur
Power requirement	0.05kWh/m^3 gas

State of development The process has been adopted recently in about 60 plants in Japan including Mitsubishi Chemical's Sakaide plant, where it treats 85,000Nm^3/hr coke oven gas and Sumitomo Metal's Wakayama plant, for treatment of 200,000Nm^3/hr coke oven gas.

The process has undergone improvement recently. The improved process will be used for Nippon Steel's Nagoya plant, where a unit is being built to treat 400,000Nm^3/hr coke oven gas.

Economics The Takahax process and the Thylox process are compared below with regard to investment and operation costs. The investment cost for treating 10,000m^3/hr for 5g/m^3 H_2S by the Takahax process is as follows:

Remote-control system	¥70,930,000
Field operation system	¥62,890,000

On the other hand, the Thylox process costs ¥94,370,000, or about 40% more. The operation cost per cubic meter of raw gas calculated from fixed and variable costs is:

Takahax process	about ¥0.23
Thylox process	about ¥0.46

The Thylox process requires an additional expenditure of ¥0.21 or so for arsenic removal.

Advantages:

Both investment and operation costs are low.

Very high recovery of H_2S--more than 99.8%--is attained.

Operation is so easy that unattended operation is possible.

The catalyst is not poisonous, so that the by-product sulfur is useful.

Possible application The Takahax process has so far been utilized chiefly in the town gas industry and iron industry, especially for the desulfurization of coke oven gas. Since the catalyst is highly stable and active, the process is thought to be applicable to various gases regardless of the concentration of hydrogen sulfide, for example for the recovery of hydrogen sulfide from hydrodesulfurization of heavy oil as well as the sulfide in tail gas of Claus furnace. Also in treating waste fermentation gas, the process is utilized to give methane gas which may be used as a heat source for boilers.

The Takahax process may be helpful in removing heavy metals in wastewater by using hydrogen sulfide which is quite effective in precipitating heavy metals but has not been used for that purpose because of the difficulty in treating the gas released to the air.

4.14 Other wet processes[11)]

Sodium hypochlorite process Hitachi Shipbuilding & Engineering Co. has operated recently a pilot plant (500Nm^3/hr gas) to absorb SO_2 with a sodium hypochlorite solution which oxidizes SO_2 and converts it to sulfuric acid. Limestone is added to precipitate gypsum. The remaining sodium chloride solution is subjected to electrolysis to regenerate the hypochlorite.

Magnesium hydroxide process Tsukishima Machinery Co. has developed a wet process using magnesium hydroxide slurry. The details have not been published yet.

5 Waste-gas desulfurization by dry process

5.1 Mitsubishi DAP-Mn process[11, 17]

Developer Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Description Activated manganese oxide $MnO_x \cdot nH_2O$ in powder form (5 to 150 microns in size) is charged into an absorber, and is dispersed and carried by flue gas. The powder is caught by a multiclone and electrostatic precipitator with an efficiency of 99.99%. The total pressure drop of the gas is 100 to 150mm H_2O. About 90% of SO_2 in the gas is removed forming magnesium sulfate. The powder caught is a mixture of the oxide and sulfate. Most of the powder is returned to the absorber. The rest is treated with water to dissolve the sulfate; the unreacted oxide which is insoluble in water is centrifuged and returned to the absorber. The manganese sulfate solution is treated with ammonia and air to precipitate activated manganese oxide. The mother liquor is concentrated to obtain solid ammonium sulfate which has more than 99% purity.

State of development A prototype plant to treat 150,000Nm^3/hr flue gas from an oil-fired boiler was completed at Yokkaichi, Chubu Electric Power, in 1967 under contract with the Agency of Industrial Science and Technology. A semicommercial plant to treat 330,000Nm^3/hr gas (110MW equivalent) has been completed recently at Yokkaichi.

Economics The investment cost for the semicommercial plant (110MW) is ¥1.4 billion. The desulfurization cost would ~~exceed~~ be about ¥2,000 per kiloliter oil.

Advantages

The absorbent, which is highly reactive and in powder form, enables SO_2 to be recovered at a high rate.

Pressure drop through the absorber is only 10 to 20mm H_2O. The total pressure drop does not exceed 150mm H_2O.

Temperature drop in the gas is also small. The gas temperature after desulfurization is kept above 110°C.

Disadvantages

The desulfurization cost is relatively high.

Demand for ammonium sulfate is decreasing.

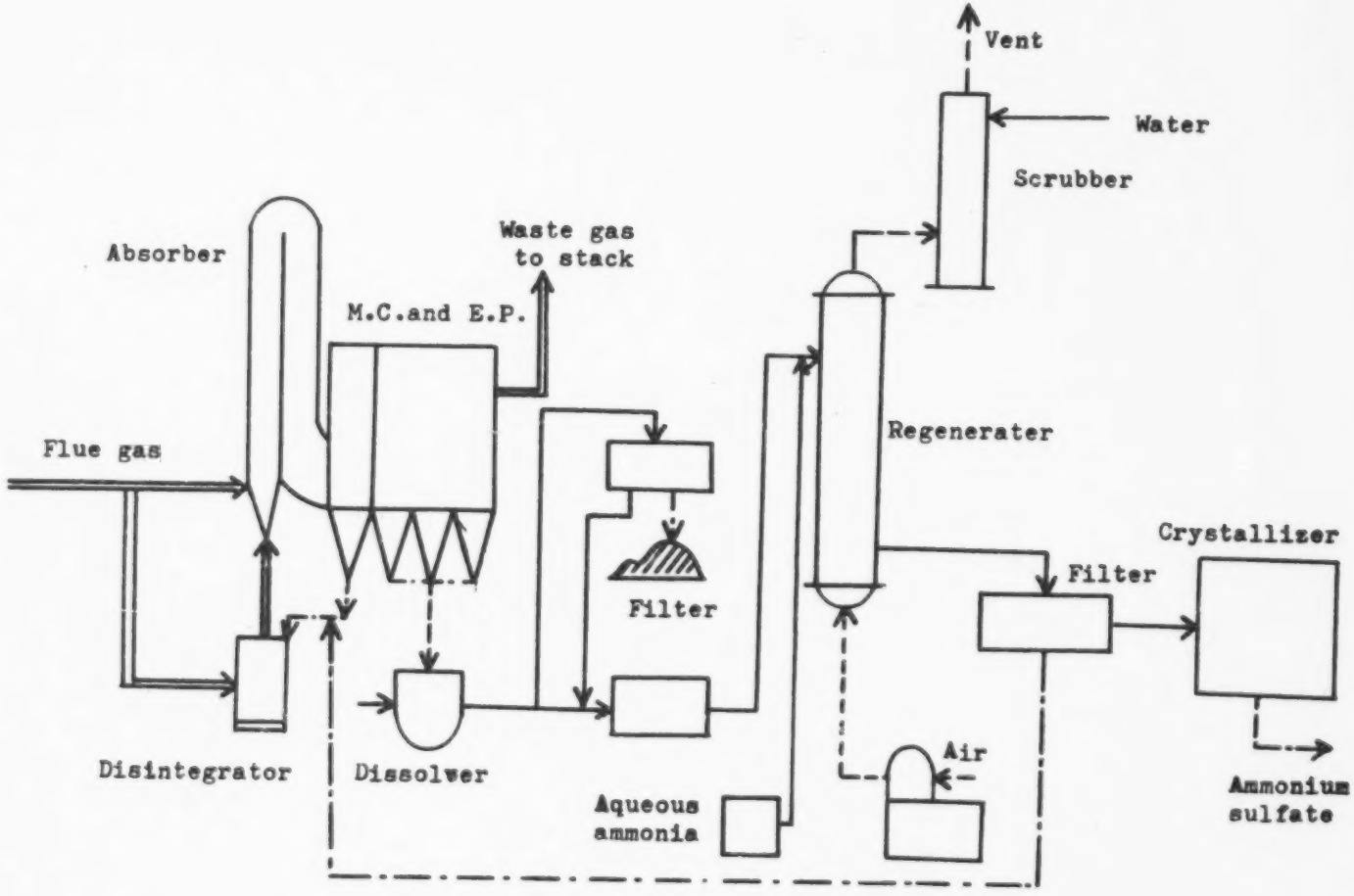


Figure 5.1 Flow sheet of activated manganese oxide process

5.2 Hitachi activated carbon process[11, 13]

Developer Hitachi Ltd.
2-8, Otemachi, Chiyoda-ku, Tokyo

Description SO_2 in flue gas is absorbed by activated carbon. The carbon is then washed with water to release dilute sulfuric acid (about 20% H_2SO_4).

State of development A prototype plant to treat ~~150~~ 150,000 Nm^3/hr flue gas from an oil-fired boiler was built in 1968 at Goi works, Tokyo Electric Power. Five towers packed with activated carbon were used alternatively for absorption, water washing, and drying. Tests on concentration of the product acid to 65% H_2SO_4 were also carried out using submerged combustion (Figure 5.2).

A semicommercial plant to treat ~~420~~ 420,000 Nm^3/hr flue gas from an oil-fired boiler (150MW equivalent) is under construction at Kashima works, Tokyo Electric Power at a cost of ¥1.7 billion. The plant will be put into operation by September 1972. Six towers with three compartments each are used in two trains. (Three towers with nine compartments form one train). The gas from electrostatic precipitators containing 800ppm SO_2 and less than 30mg/Nm^3 of dust at a temperature of 135°C will be introduced in the absorbers to remove 80% of SO_2 while maintaining the outlet gas temperature above 100°C. Dilute sulfuric acid (20% H_2SO_4) will be produced at a rate of 5.9 tons/hr which will be treated with powdered limestone to produce salable gypsum at a rate of 2.3 tons/hr. The plant will consume 3,900kW power, 1.2 ton/hr of limestone and 25 tons/hr of water.

Advantages

The temperature of the desulfurized gas is kept above 100°C.

The process is simple and operation is easy.

The dust in the gas adhered to the carbon is washed away with water to maintain the activity of the carbon.

By-product gypsum is of good quality and salable.

Disadvantages

Investment cost is relatively high.

Oversupply of gypsum is likely several years from now.

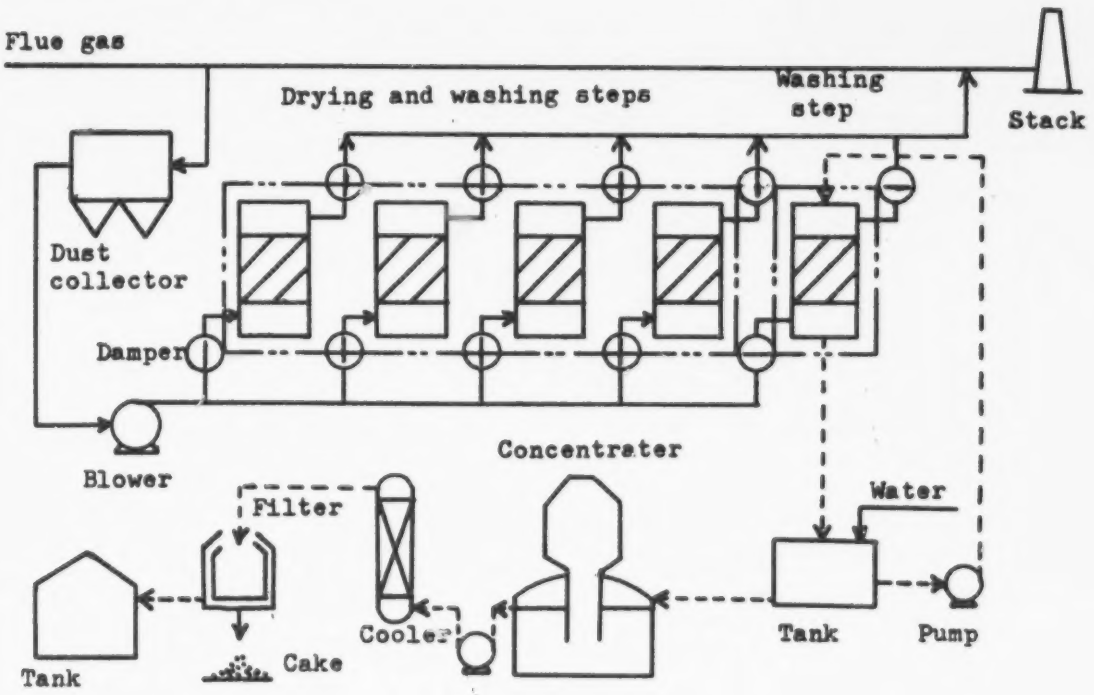


Figure 5.2 Flow sheet of Hitachi process (150,000Nm^3/hr)

5.3 Sumitomo activated carbon process[12, 13)]

Developer Sumitomo Shipbuilding and Machinery Co. Ltd.
2-1, 2-chome, Otemachi, Chiyoda-ku, Tokyo

Description Moving beds of activated carbon are used for SO_2 recovery. The flow sheet is shown in Figure 5.3. Granular activated carbon descends slowly through an absorber into which flue gas is introduced perpendicularly to the carbon stream. The carbon which absorbed SO_2 is discharged from the bottom of the absorber and is led into a desorber through which the

carbon again descends slowly. A recyling gas heated in a heat exchanger is introduced into the desorber perpendicularly to the carbon stream for desorption. An inert gas or reducing gas is introduced to purge the SO_2 gas. SO_2 concentration in the purged gas is controlled between 10 and 20%. A portion of the purged gas is led to a sulfuric acid plant; the rest is recycled to the desorber after being heated in the heat exchanger. Tail gas from the sulfuric acid plant which contains SO_2 is introduced into the absorber.

State of development A pilot plant to treat 10,000Nm^3/hr flue gas was built in 1968. A prototype plant to treat 175,000Nm^3/hr gas was built recently at Amagasaki works, Kansai Electric Power Co.

Advantages

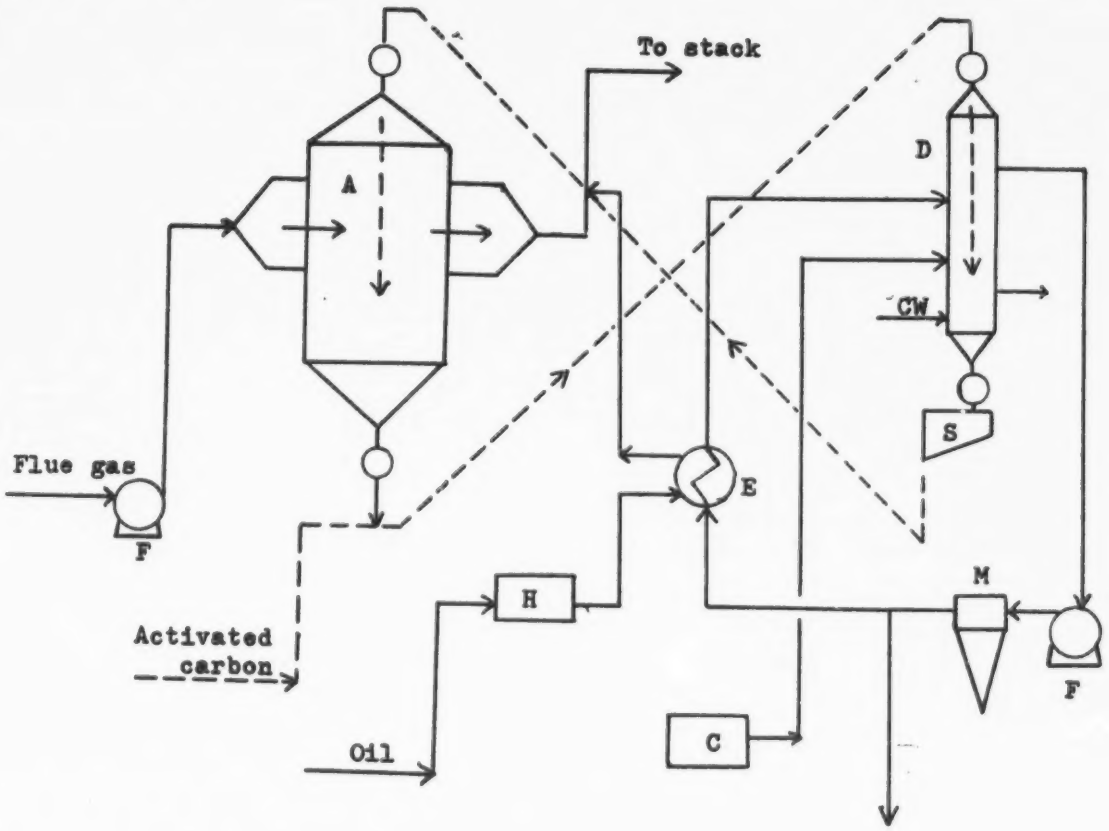
The process is fairly simple and is operated safely.

The continuous cross-flow of gas and carbon ensures a high efficiency of absorption and desorption.

Disadvantages

Carbon consumption is considerably high.

The desulfurization cost may be high as well.



——→ Gas - - - - → Activated carbon

A : Absorber C : Converter CW : Cooling water
D : Desorber E : Heat exchanger F : Fan
H : Hot-air furnace M : Multiclone S : Vibrating screen

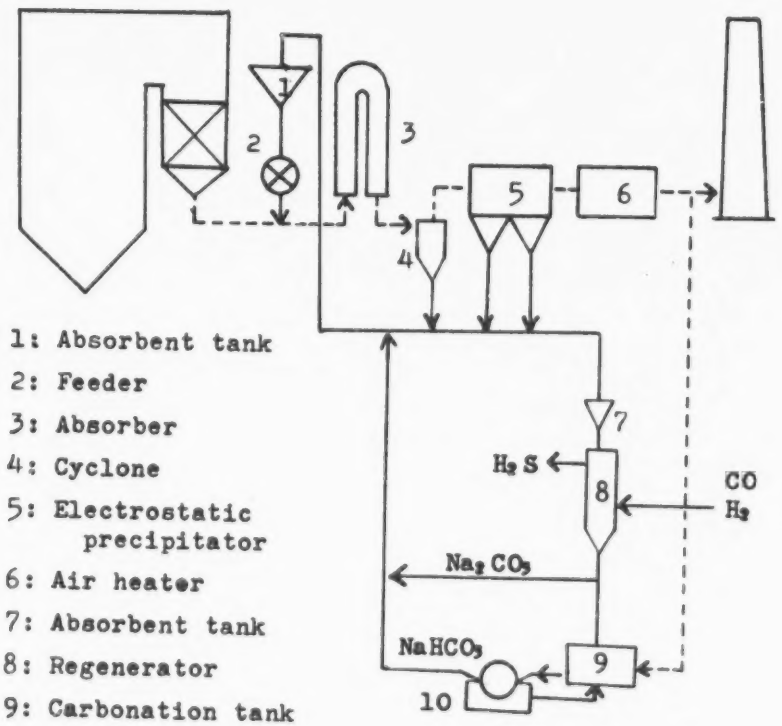
Figure 5.3 Flow sheet of Sumitomo Shipbuilding - Kansai Electric process

5.4 NRIPR active sodium carbonate process[11, 13)]

Developer National Research Institute of Pollution and Resources
188, Kotobukicho, Kawaguchi-shi, Saitama Prefecture

State of development Pilot plant tests were carried out, desulfurizing 150 to 200Nm³/hr flue gas. Tests on regeneration are in progress.

Description An absorber in the form of an inverted U 15.5cm in diameter and 25 meters in length is used in the pilot plant. Light-weight soda ash (or sodium bicarbonate) in powder form is charged into the absorber and carried by the flue gas at a temperature between 300 and 350°C and a velocity of 5 meters/sec. About 110 to 120 grams of sodium carbonate is charged per Nm^3 gas. Nearly 90% of SO_2 is removed by reaction with the carbonate. The reacted powder which is a mixture of sodium sulfate and carbonate is caught by sedimentary and electrostatic precipitators. Most of the powder is returned to the absorber; the rest is subjected to regeneration.



1: Absorbent tank
2: Feeder
3: Absorber
4: Cyclone
5: Electrostatic precipitator
6: Air heater
7: Absorbent tank
8: Regenerator
9: Carbonation tank
10: Filter

Figure 5.4 Flow sheet of NRIPR sodium carbonate process

The regeneration tests have been carried out by using a melt reduction process. The powder is charged into a hot reducing gas obtained by partial combustion of oil. Sodium sulfate is reduced rapidly to form molten sodium sulfide. The sulfide is then treated with steam and carbon dioxide at about 400°C to recover soda ash.

$$Na_2S + H_2O + CO_2 = Na_2CO_3 + H_2S$$

It is also possible to carry out this reaction in an aqueous solution. Sodium carbonate thus regenerated is returned to the absorber. Hydrogen sulfide can be converted into sulfur by a conventional process.

Advantage and disadvantage High recovery of SO_2 can be attained due to the high reactivity of the light-weight soda ash. The regeneration process is not simple and seems to be fairly expensive.

5.5 Shell process (Cupric oxide process)[11,13]

Constructor Japan Shell Technology Co.

User Showa Yokkaichi Sekiyu, Yokkaichi Plant

Description SO_2 in flue gas at 400°C is absorbed by cupric oxide held by an alumina carrier. The cupric sulfate thus formed is then reduced with hydrogen to release SO_2 and regenerate the cupric oxide.

$$CuO + SO_2 + 1/2\ O_2 = CuSO_4$$
$$CuSO_4 + H_2 = CuO + SO_2 + H_2O$$

Two towers packed with the cupric oxide-alumina absorbent are provided, the two alternating between absorption and regeneration every hour.

State of development A plant with a capacity to treat 120,000Nm^3/hr flue gas from an oil-fired boiler will be built by March 1973 at the Yokkaichi refinery, Showa Yokkaichi Sekiyu Co. The SO_2 gas recovered will be led into a Claus furnace to react with hydrogen sulfide gas from the refinery to produce elemental sulfur. This plant will be the world's first commercial plant to use the Shell process; Shell has made pilot plant tests in the Netherlands to treat 1,000Nm^3/hr gas.

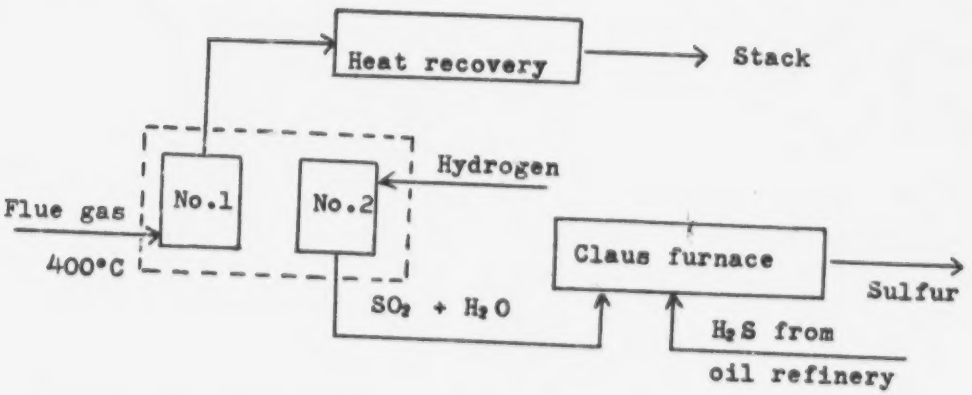


Figure 5.5 Flow sheet of Shell process

5.6 Other dry processes[11)]

Hitachi Shipbuilding activated carbon process Hitachi Shipbuilding & Engineering Co. operated a pilot plant in 1970 to treat 1,500Nm^3/hr gas. A moving bed of activated carbon was used for desulfurization. The carbon was then heated to 300°C and treated with superheated steam to desorb SO_2, and then treated with air at 150 to 200°C to recover activity. Hitachi Shipbuilding gave up the process because of the high desulfurization cost.

Reduction process Hitachi Shipbuilding & Engineering Co. has made bench-scale tests of a reduction process which was originally developed by Shevron Chemical. Reacting with carbon monoxide in the presence of a catalyst, SO_2 is reduced to elemental sulfur. Nitrogen oxides are reduced to nitrogen at the same time.

IFP process Nippon Oil has recently installed a commercial plant using the IFP process for removal of H_2S in the tail gas from a Claus furnace. It is said that the process is similar to the Claus process except for the use of a special catalyst.

6 Economic aspects

6.1 Supply, demand, and price of sulfur and its compounds

Supply and demand In 1970 supply of sulfur and its compounds totaled nearly 2.9 million tons as sulfur (Table 6.1). Pyrite was the major source of sulfur. Production of sulfuric acid registered nearly 7 million tons (nearly 2.3 million tons as sulfur). About 60% of the acid was produced from pyrite and about 40% from smelter gas. The supply of pyrite will decrease year by year with the increase of smelter gas.

Table 6.1 Estimated supply of and demand for sulfur and its compounds (1,000 tons as sulfur)[3]

	1970	1971	1972	1973	1974	1975
Supply						
Pyrite	1,475	1,465	1,427	1,376	1,315	1,245
Smelter gas	1,042	1,233	1,338	1,508	1,693	1,890
Mined sulfur	109	56	36	0	0	0
Recovered sulfur*	270	375	570	608~942	763~1,282	795~1,625
Total	2,896	3,151	3,277	3,513~3,847	3,766~4,285	3,930~4,787
Demand						
Sulfuric acid	2,289	2,428	2,525	2,626	2,731	2,840
Elemental sulfur	326	335	342	348	357	365
SO_2 (liquid)	150	155	160	160	160	160
Other*	108	138	169	211	255	305
Total	2,873	3,056	3,196	3,345	3,503	3,670
Surplus	23	73	79	137~481	263~782	260~1,117

* Including by-products of waste-gas desulfurization

Mined sulfur is scanty and decreasing. Recovered sulfur and its compounds by-produced from hydrodesulfurization of oil and waste-gas desulfurization will increase remarkably and reach about 1 million tons as sulfur by 1975.

The consumption of sulfur and its compounds is expected to increase by about 5% yearly. Considerable amounts of by-products from waste-gas desulfurization will be utilized. For example, in 1975 nearly 1 million tons of gypsum (about 180,000 tons as sulfur) obtained from waste-gas desulfurization is expected to be used for cement and wall board. The demand for sodium sulfite is estimated to increase from 370,000 tons in 1970 to 590,000 tons in 1975. Still a considerable oversupply of sulfur and its compounds is expected in the near future due to the increase of desulfurization plants. Sodium sulfite is already reported to be in overproduction.

Price of sulfur and its compounds

Demand for and price of sulfur and its compounds in Japan in 1969 are shown in Table 6.2. The prices of sulfuric acid and elemental sulfur were slightly higher in 1970 but was considerably lowered in 1971 due to an oversupply. It seems that the prices of sulfur and its compounds would continue to decrease in future.

Table 6.2 Demand and price of sulfur and its compounds in 1969[18)]

	Demand (1,000 tons of material)	Price (¥/ton)
Sulfuric acid	6,800	8,000
Elemental sulfur	380	21,500
Gypsum	3,510	3,000 to 5,000
Sodium sulfate	400	16,500 to 17,000
Sodium sulfite	180	10,000 to 30,000
Ammonium sulfate	1,200	14,000
Liquid SO_2	10 to 20	30,000

6.2 Cost of hydrodesulfurization

Topped-crude hydrodesulfurization The investment and operation costs for a topped-crude hydrodesulfurization plant with a capacity of 50,000-BPSD was reported as follows.[5)]

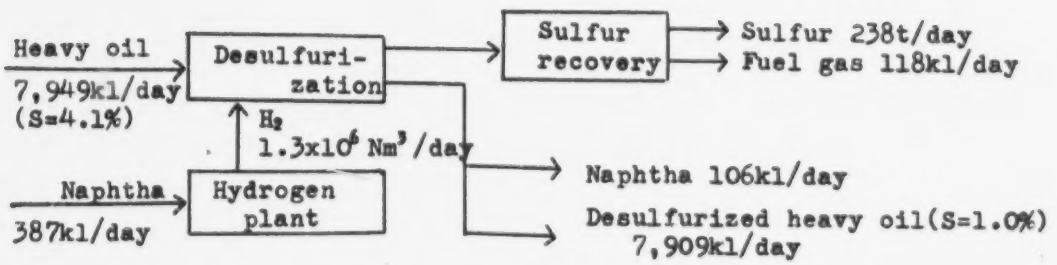


Figure 6.1 Material balance in topped-crude hydrodesulfurization (Khafji heavy oil 50,000BPSD)

Table 6.3 Investment cost for topped-crude hydrodesulfurization plant (50,000 BPSD) (millions of yen)

	Desulfurization	Hydrogen production	Sulfur recovery	Total
Equipment	6,350	1,600	490	8,440
Patent fee	1,020	169	17	1,206
Catalyst, chemicals	781	151	22	954
Land	140			140
Total	8,291	1,920	529	10,740

Table 6.4 Operation cost for topped-crude hydrodesulfurization plant (50,000 BPSD) (¥1,000/day)

	Desulfurization	Hydrogen production	Sulfur recovery	Total
Fixed cost*	7,220	1,770	470	9,460
Variable cost	6,540	4,650	-220	10,970
Subtotal	13,760	6,420	250	20,430
By-product credit**	-1,770	-	-2,620	-4,390
Total	11,990	6,420	-2,370	16,040

* Operation 70% of total hours (about 6,100 hours a year)

** Naphtha ¥6,000/kl; Sulfur ¥11,000/ton

Desulfurization cost is calculated as ¥2,020/kiloliter Khafji heavy oil when the plant is operated for 70% of total hours (about 6,100 hours a year) and about ¥1,870 when operated for 80% (about 7,000 hours a year). The price of high-sulfur heavy oil (sulfur 3 to 4%) is about ¥5,000/kiloliter and that of desulfurized heavy oil (sulfur 1 to 1.5%) is about ¥6,500. The difference by the desulfurization is less than the desulfurization cost. To encourage oil refiners to practice desulfurization, the Japanese Government subsidizes the refiners at a rate of ¥500 per kiloliter oil subjected to desulfurization.

Vacuum gas-oil desulfurization The investment and operation costs for a vacuum gas-oil hydrodesulfurization plant with a capacity of 50,000-BPSD of Khafji heavy oil are as follows:[5]

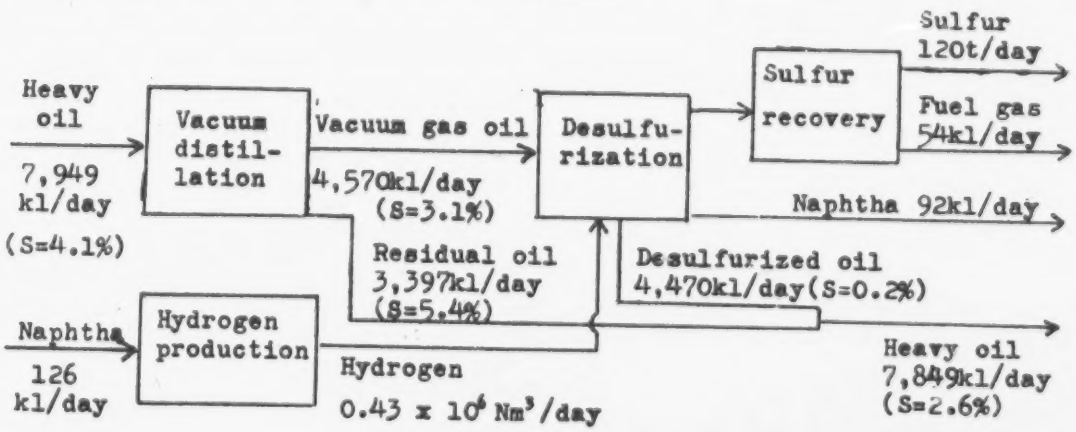


Figure 6.2 Material balance in vacuum gas-oil hydrodesulfurization (Khafji heavy oil 50,000BPSD)

Table 6.5 Investment cost for vacuum gas-oil hydrodesulfurization plant (50,000 BPSD) (millions of yen)

	Vacuum distillation	Desulfurization	Hydrogen production	Sulfur recovery	Total
Equipment	1,170	2,700	816	322	5,008
Patent fee	0	300	55	6	361
Catalyst, chemicals	0	108	49	11	168
Land		140			140
Total	1,170	3,248	920	339	5,677

Table 6.6 Operation cost of VGO hydrodesulfurization (¥1,000/day)

	Vacuum distillation	Desulfurization	Hydrogen production	Sulfur recovery	Total
Fixed cost*	900	2,480	740	260	4,380
Variable cost	950	930	1,520	-80	3,320
Subtotal	1,850	3,410	2,260	180	7,700
By-product credit**	0	-1,000	0	-1,320	-2,320
Total	1,850	2,410	2,260	-1,140	5,380

* Operation 80% of total hours (about 7,000 hours a year)

** Naphtha ¥6,000/kl; Sulfur ¥11,000/ton

The desulfurization cost is calculated as ¥680 per kiloliter of heavy oil or ¥1,180 per kiloliter of vacuum gas oil to be subjected to desulfurization. The Japanese Government offers subsidies of ¥500 per kiloliter of vacuum gas oil subjected to desulfurization. Although desulfurization cost is much lower for VGO desulfurization than for TC desulfurization, the use of residual oil from vacuum distillation poses a big problem as has been mentioned already (3.5).

6.3 Cost of flue-gas desulfurization

Desulfurization costs for six flue-gas desulfurization processes are compared in Table 6.7. Among them, only the Wellman-Lord process and Kureha process are now in commercial operation. Therefore, the data in the table may not be quite accurate. The table indicates that desulfurization cost is less for wet processes than for dry processes.

Table 6.7 Comparison of desulfurization costs[12)]

	Wet process			Dry process		
	Kureha	Wellman-Lord	Chemico	Hitachi carbon	Mitsubishi manganese	Sumitomo carbon
Power plant (MW)	100	250	1,200	250	250	58
Amount of gas (1,000Nm^3/hr)	300	750	3,600	750	750	174
Sulfur in oil(%)	2.8	3.0	3.3	3.0	3.0	2.0
Sulfur removal (%)	95	90	80-90	80	80	80
Investment cost (billions of yen)	0.42	1.14	4.0	2.4	1.9	0.85
By-product	Na_2SO_3	H_2SO_4	H_2SO_4	H_2SO_4**	$(NH_4)_2SO_4$	H_2SO_4
Desulfurization cost(¥/kl oil)*	500	870	780	1,300	1,100	2,560

* Including depreciation for 7 years.

** Gypsum is produced with the acid.

Desulfurization cost is the lowest for the Kureha process, which by-produces sodium sulfite. Supply of sodium sulfite, however, is already in excess of demand in Japan. Although gypsum and concentrated sulfuric acid are more advantageous by-products at present, those compounds as well as elemental sulfur are likely to be in oversupply sooner or later. In discarding the by-product in the most harmless form, gypsum may be the best choice because it is least reactive.

6.4 Cost comparisons of oil desulfurization and flue-gas desulfurization

The costs of fuels containing different amounts of sulfur with or without desulfurization are compared in Table 6.8.[19)] The table indicates that flue-gas desulfurization is advantageous over hydrodesulfurization because of its lower cost and higher sulfur removal. The use of asphalt(residue of vacuum distillation) for fuel accompanied by flue-gas desulfurization seems to be promising if asphalt can be handled without difficulty. Hydrodesulfurization has advantages over the use of low-sulfur crude oil (Minas) and LNG, both of which are fairly expensive in Japan.

Gasification desulfurization of oil (3.6 and 3.7) might be a little more costly than hydrodesulfurization, but higher sulfur removal is attained.

Both hydrodesulfurization and flue-gas desulfurization are likely to continue their present rapid growth in Japan for a few more years; in the meantime gasification desulfurization of oil is expected to be commercialized. The situation may take a turn several years from now, when oversupply of sulfur and its compounds assumes serious proportions.

Table 6.3 Cost of fuel and desulfurization (2,000MW power plant. Fuel consumption is 2,730 million liters of oil or 2,900 million Nm^3 of LNG yearly)[19]

	Topped-crude hydrodesulfurization		Flue-gas desulfurization(A)		Without desulfurization		
	Kuwait heavy oil	Khafji heavy oil	Khafji heavy oil	Khafji asphalt	Heavy oil (Standard)	Minas crude oil	LNG
Sulfur in fuel (%)	3.1	4.1	4.2	5.5	2.0	0.1	0
Sulfur removal (%)	74	76	90	93	0	0	0
SO_2 in flue gas (ppm)	600	600	250	250	1,200	60	0
Cost of fuel (Yen/kl or Nm^3)	5,000	5,000	5,000	4,000	6,000	7,000	8.5
Cost of fuel (Billion yen/year) (B)	13.65	13.65	13.65	10.92	16.38	19.11	24.65
Investment cost (Billions of yen)	9.97	10.74	10.10	11.23	0	0	6.0
Desulfurization cost (Billion yen/year)(C)	5.34	6.16	4.78	5.72	0	0	1.88
Total cost (B + C) (Billion yen/year)(D)	18.99	19.81	18.43	16.64	16.38	19.11	26.53
By-products credit (Billion yen/year)(E)	1.24	1.46	1.52	2.08	0	0	0
Net cost (D - E) (Billion yen/year)	17.75	18.35	16.91	14.56	16.38	19.11	26.53

(A) By Wellman-Lord process

(C) Including 23% of investment cost

(19)

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